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XVIII.—CAMPHORIC ACID.

[NINTH PAPER.]

STRUCTURE AND CONFIGURATION OF CISTRANSCAMPHOLYTIC ACID.

BY WILLIAM A. NOYES AND EDWARD F. PHILLIPS.

The opinion has been expressed by one of us[1] that cistranscampholytic acid and ciscampholytic acid (isolauronolic acid) are stereoisomeric bodies having the same structural formula. Walker[2] has recently expressed the same opinion as to the relation between the two acids, and has shown that each may be transformed into the other by means which seem to preclude any other explanation than that of stereoisomerism.

While we still hold the same opinion as to the structure of these acids, we have found that in one important point Walker and Cormack[3] have been led to a wrong conclusion. The cistranscampholytic acid obtained by the decomposition of dihydroaminocampholytic acid with nitrous acid[4] is optically active, $[\alpha]_D = -59°.6$ at 18°. The method of electrolysis used by Walker and Cormack evidently gives a small amount of the same acid, as they obtained the value $[\alpha]_D = -5°$ with the acid at first prepared. The acid which they obtained indirectly from ciscampholytic acid[1] is, probably, a racemic mixture of the right and left forms of the acid.

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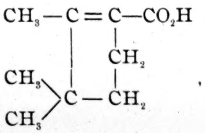
[1] This JOURNAL, **17**, 423; **23**, 134; Ber. d. chem. Ges., **28**, 551; **33**, 57.

[2] J. Chem. Soc., **77**, 383.

[3] *Loc. cit.*, p. 377.

[4] This JOURNAL, **17**, 424.

In his discussion of the optical properties of cistranscampholytic acid Walker assumes that an acid having the structural formula,



must necessarily be inactive because there is no single asymmetric carbon atom in the compound. For the ciscampholytic acid (isolauronolic acid) this conclusion is correct, since in that acid the methyl and carboxyl groups lie in the plane of the ring and that plane becomes one of perfect symmetry, the right and left sides being exactly alike. For such a body two optically opposite forms are impossible. This conclusion is in entire agreement with the results obtained by Blanc,[2] who has shown that ciscampholytic acid cannot be separated into two optically active forms. For the benefit of those who still hold to Bredt's formula for camphor it may be worth while to remark that the formula for ciscampholytic acid given above is the only one thus far proposed which does not imply that the acid is racemic instead of inherently inactive.

If we assign to dihydroaminocampholytic acid the configuration,[3]

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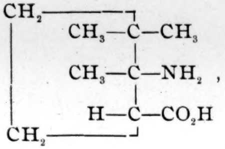
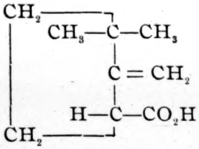
[1] *Loc. cit.*, p. 380.

[2] Bull. Soc. Chim., **21**, 832.

[3] This formula is based on the configuration for camphoric acid proposed some years ago by Aschan, which represents it as a "cis" compound. See Aschan: Ber. d. chem. Ges., **27**, 2002; Noyes: This JOURNAL, **17**, 424; Ber. d. chem. Ges., **28**, 551. Walker (J. Chem. Soc., **77**, 395) has recently expressed the same view of the configuration of the acid, but appears to have overlooked the older statements.

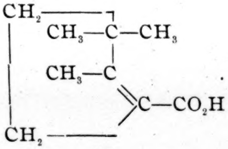


only two formulæ appear possible for the cistranscampholytic acid, which is formed from it by the loss of the elements of ammonia, on treatment with nitrous acid. These are :



I.

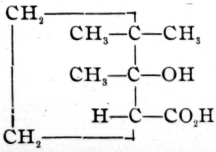
and



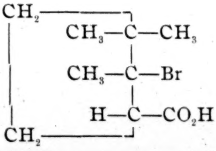
II.

The first of these formulæ has been proposed by Blanc[1] and Bouveault.[1] It appears to be entirely inconsistent with the conduct of the dibromide and hydrobromide of the acid as studied by Walker[2] and myself. The following facts also furnish, as it seems to us, incontestible evidence against the formula.

Dihydrohydroxycampholytic acid gives a brom acid on treatment with cold aqueous hydrobromic acid. These compounds should have the configuration :



and



Both show strong right-handed rotation toward polarized light, as do also the dihydroaminocampholytic acid and the original camphoric acid (see experimental part). When cistranscampholytic acid, which has a left-handed rotation, is treated with aqueous hydrobromic acid, a brom acid is obtained which not only has the same melting-point,[1] or rather temperature of decomposition, but we have now shown that it has also a right-handed rotatory power which is almost identical with that of the brom acid obtained from the hydroxy acid. The two brom acids are, undoubtedly, identical both in structure and in configuration.

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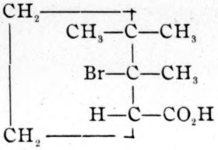
[1] Private communications.

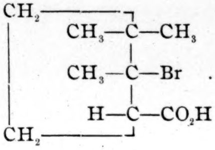
[2] J. Chem. Soc., **77**, 379, 382.

As Walker[2] has pointed out, an acid having the structure represented by formula I above would, from all that we know of similar compounds, add the bromine of the hydrobromic acid to the methylene group. If, however, for the sake of argument, we admit that in the present case the bromine *may* attach itself to the carbon atom of the ring, two compounds of opposite configuration would be formed; *viz.*,



$$\begin{array}{l} CH_2 \\ \quad CH_3-C-CH_3 \\ \quad Br-C-CH_3 \\ \quad H-C-CO_2H \\ CH_2 \end{array}$$

and



$$\begin{array}{l} CH_2 \\ \quad CH_3-C-CH_3 \\ \quad CH_3-C-Br \\ \quad H-C-CO_2H \\ CH_2 \end{array}$$

.

Even if we should suppose that, on account of the interference of the carboxyl on one side of the ring, the addition of the hydrobromic acid takes place chiefly on the opposite side, the first configuration indicated above would result. But this configuration is the opposite of that of the hydroxy acid. Hence, on any reasonable supposition which we have been able to make, Blanc's formula for cistranscampholytic acid is impossible.

It will be objected to formula II, which we propose for the acid, that it contains no asymmetric carbon atom and that, according to this formula, the acid should be optically inactive. Walker appears to take this view, and, if we assume that the carboxyl and methyl groups lie in the plane of the ring, and that one or the other of the groups lies within the ring, the compound would have a plane of symmetry and would be inactive. Such a supposition appears to the writer extremely improbable; partly because, for geometric reasons, there would not seem to be room for one of these groups within the ring; partly because, in accordance with Baeyer's theory of tension within polymethylene rings, another position for the atoms is found which implies far less tension than that just considered. This other position is indicated, somewhat imperfectly, by the manner in which formula II is written. By this method of writing it is intended to indicate that the doubly united carbon atoms no longer lie exactly in the plane of the other three atoms of the ring, but are thrown slightly out of that plane, the one on one side, the other on the other. The carboxyl and methyl groups connected with the same atoms will, in such a case, lie on opposite sides of the ring. A compound of this configuration has no plane of symmetry and may exist in a right-handed and a left-handed form.

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[1] This JOURNAL, **17**, 427. This older observation and its significance seem to have been overlooked by Blanc and Walker.

[2] *Loc. cit.*, p. 382.

So far as we are aware, no previous case is known in which an optically active body is formed by the addition of a halogen acid to an unsaturated compound, in which the only asymmetric carbon atoms present are those which become asymmetric through the addition of the halogen acid. In all other cases which have been studied the halogen may add itself equally on both sides of the double union and racemic mixtures are formed. An examination of the formula proposed for cistranscampholytic acid suggests a simple explanation for its remarkable conduct. In that formula the double union is accessible to the hydrobromic acid only on the outside, the other side of the double union being directed toward the inside of the ring and protected from the approach of the hydrogen and bromine; but the addition of the hydrobromic acid on the outside produces the configuration which corresponds to that of the hydroxy acid and of the original camphoric acid.

While the explanation given for the optical activity of the cistranscampholytic acid appears to be a logical development of current theories of stereomeric structure, the compound is at present the only one known[1] of an optically active body containing no asymmetric carbon atom in the ordinary sense.[1] The case is so peculiar and important from the theoretical standpoint, that it will be made, if possible, the subject of a more careful and extended study.

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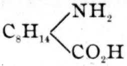
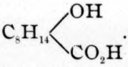
[1] Some years ago Baeyer (Ber. d. chem. Ges., **27**, 455) suggested that the activity of limonene might be due to a double union in a cyclic compound but another structure has now been assigned to the body. For other cases, in which optical activity has been erroneously ascribed to unsaturated compounds, see Bischoff and Walden, "Stereochemie", p. 841.

EXPERIMENTAL PART.

Dihydroaminocampholytic Acid,  $C_8H_{14}\langle{}^{NH_2}_{CO_2H}$. — This was prepared by the methods previously described.[2] Two determinations of the solubility gave 7.4 and 7.8 parts dissolved by 100 parts of water at 20°.

The saturated solution gave :

$$[\alpha]_{\mathrm{D}} = +53^\circ.7.$$

Dihydrohydroxycampholytic Acid,  $C_8H_{14}\langle{}^{OH}_{CO_2H}$.—The dihydroaminocampholytic acid was decomposed by treatment with dilute sulphuric acid and sodium nitrite,[3] the cistranscampholytic acid and the hydroxy acid were partly separated by ligroin, and the latter was crystallized from water or from acetic ether.

For the acid crystallized from water, 100 parts of water dissolved at 20°, 1.97 parts and for the saturated aqueous solution,

$$[\alpha]_{\mathrm{D}} = +72^\circ.05.$$

For the acid crystallized from acetic ether, 100 parts of water dissolved 2.14 parts at 20° and gave :

$$[\alpha]_{\mathrm{D}} = +71^\circ.55.$$

Cistranscampholytic Acid, $C_8H_{13}CO_2H$.—The acid which was obtained by extraction with ligroin was distilled with steam, the cistranscampholytic acid which passed over was taken up with ligroin and, after distilling most of the ligroin on the water-bath, the remainder was removed and the acid was dried by heating it on the water-bath, while the bulb containing it was evacuated.

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[1] In one sense two asymmetric carbon atoms are present, since the two sides of the double union are unlike.

[2] This JOURNAL, **16**, 503.

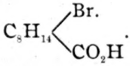
[3] *Ibid.*, **17**, 424.

The acid obtained in this manner gave the following values for specific gravity and for specific rotatory power:

Temperature.	Specific gravity.	$[\alpha]_D$.
13°.2	1.0166	—60°.4
18°	1.0145	—59°.6
27°.5	1.0107	—58°.0

A portion of the acid which was distilled under diminished pressure gave $[\alpha]_D = -53^\circ.9$, indicating that distillation may cause the conversion of a part of the acid into the racemic form or into cistranscampholytic acid.

β-Bromdihydrocampholytic Acid,



$C_8H_{14}\langle^{Br.}_{CO_2H}$. — This was prepared from the cistranscampholytic acid by putting 2 grams of the acid in a small glass-stoppered bottle, adding a little ligroin and 8–10 cc.of fuming hydrobromic acid, and shaking for a few minutes. Enough ligroin was then added to dissolve the brom acid, and the ligroin solution was separated and dried with sodium sulphate. The solution was then evaporated immediately in a vacuum desiccator by continuous evacuation. The crystals obtained were dissolved in cold ligroin and recrystallized in the same manner.

From the dihydrohydroxycampholytic acid the brom acid was prepared and crystallized in essentially the same manner.

The brom acid obtained from the cistranscampholytic acid gave, in a 10 per cent solution in benzene:

$$[\alpha]_D = +89^\circ.6 \text{ and } 91^\circ.5.$$

The brom acid obtained from the dihydrohydroxycampholytic acid gave, under the same conditions:

$$[\alpha]_D = +93^\circ \text{ and } 94^\circ.$$

While the agreement is not exact, when we consider the ease with which cistranscampholytic acid passes over into ciscampholytic acid when treated with mineral acids, and, further, that the compound was prepared in the first case from a body with a negative rotation of 59°, and in the second case from one with a positive rotation of 72°, there seems to be no reasonable ground for doubting the identity of the acid from the two sources.

A NEW METHOD FOR THE DETERMINATION OF ALUMINIUM.

By E. T. Allen and V. H. Gottschalk.

In the course of some experimental work requiring many determinations of aluminium, we became impressed with the tediousness of the ordinary method. Fortunately, the majority of cases where aluminium is to be determined involve its precipitation together with iron. The greater the proportion of iron the denser and more readily filtered is the precipitate, but when aluminium is unaccompanied by iron, and especially when the percentage is high, the slowness with which the precipitate settles, the difficulty involved in washing it completely, the small quantity which can be successfully handled at once, and the danger of loss by solution, all conspire to make the determination a troublesome one. We made some effort to improve the ammonia method, but without any very marked success.

We compared the precipitate formed by ammonia with that formed by other reagents; ammonium carbonate and ammonia, ammonium sulphide and ammonia, ammonium phosphate and ammonia, but it did not appear to us that any of the above possessed much advantage over ammonia and ammonium chloride. The precipitates by all the above reagents are as gelatinous and difficult to filter and wash as the hydroxide by ammonia. Of Löwe's[1] method, *viz.*, the precipitation of the aluminium from a soluble aluminate by ammonium chloride, we had greater hopes, but our experience with it was a disappointment. We find the precipitate little, if any, denser than that thrown down by ammonia, while the danger of extracting silica from the glass during the considerable time necessary to boil off the ammonia, together with the well-known capacity of alumina for precipitating such substances from solution, constitute an objection to this method.

In searching for a new method, we endeavored to find an insoluble compound of aluminium which could be formed by precipitation and which is also crystalline, admitting of rapid and complete washing. The only compounds known to us which fulfilled these conditions are the crystalline hydroxide and the basic carbonate. The former is only precipitated from a soluble aluminate by the action of water:

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[1] J. B., 1860, 132; Chem. Ztg., **3**, 247.

$$MAlO_2 + 2H_2O = MOH + Al(OH)_3,$$

and this reaction is not sufficiently complete for a quantitative method. We therefore turned our attention to the basic carbonate.

Preliminary Experiments with the Basic Carbonate of Aluminium.

In our first experiments we dissolved the substance in which the aluminium was to be determined in varying quantities of water, added just enough potash or soda to redissolve the precipitate at first formed, precipitated with carbon dioxide, and then washed in various ways.[1] We were especially struck with the ease and rapidity with which the precipitates could be washed. To test the filtrates for alumina, we boiled with hydrochloric acid to decompose carbonate, added ammonia and colorless ammonium sulphide, and allowed to stand. In every case where the action of the gas had been continued for a sufficient length of time, no more alumina could be obtained from the filtrates. The results were generally somewhat high, but the error in many cases was so small and so nearly constant that we suspected it might be due to impurities precipitated from the alkali. An examination of several different samples of "C. P." caustic potash and "C. P." caustic soda proved that all, not excepting "sodium hydrate from sodium" contained silica, iron, and alumina. These impurities were carefully estimated as follows: About 20 grams of substance was weighed out of a closed flask, dissolved by distilled water, acidified, and evaporated with pure hydrochloric acid. The evaporation was performed in a platinum basin just as in an ordinary silica determination. The insoluble residue consisted of silicates, not pure silica. The filtrate was again evaporated in platinum, and in the residue the alumina and iron were determined as usual. For most of our work we selected a potash containing 0.05 per cent of the above-mentioned impurities. A considerable quantity of it was put into a glass-stoppered bottle of wide mouth and kept in the solid state. In our subsequent experiments we used weighed quantities of this potash, calculated the weight of the impurities, and assuming[1] that they were entirely precipitated with the alumina, subtracted the same from the weight of the precipitates. We chose "C. P." ammonium alum and "C. P." aluminium metal as the substances best adapted for a test of the method. The alum was carefully recrystallized and thoroughly dried in a desiccator over calcium chloride. Tested in a color cylinder, with potassium sulphocyanate, it showed no trace of iron. Below are given our results with ammonium alum, in which a correction was made for impurities in the potash. All the results are given without reserve :

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[1] A little of the precipitate adheres tenaciously to the glass. This we dissolved in hot concentrated hydrochloric acid, precipitated with ammonia, and washed on a separate filter. According to the conditions which we finally adopted (p. 302), the precipitate is boiled with water. It can then be removed entirely, without acid.

Preliminary Determinations of Aluminium in Ammonium Alum.

	Alum taken. Grams.	Al_2O_3 found. Gram.	Al_2O_3 calculated. Gram.	Difference. Milligrams.
1	1.2144	0.13737	0.13686	+0.51
2	1.0289	0.11737	0.11596	+1.41
3	1.1111	0.12550	0.12522	+0.28
4	0.9314	0.10530	0.10497	+0.33
5	1.4191	0.15921	0.15993	—0.72
6	1.1545	0.12911	0.13011	—1.00
7	1.1632	0.12966	0.13109	—1.43
8	1.3483	0.15230	0.15195	+0.35
9	1.2818	0.14460	0.14446	+0.14
10	1.6831	0.18796	0.18969	—1.73
11	1.1086	0.12648	0.12494	+1.54
12	1.0359	0.11881	0.11675	+2.06
13	1.1651	0.13229	0.13131	+0.98
14	1.0164	0.11548	0.11455	+0.93
15	1.1964	0.13482	0.13483	—0.01
16	1.1256	0.12272	0.12686	—4.14

A few of the results are decidedly low, owing probably to a slight solvent action of the wash-water, an error which we found later could be effectually guarded against. A still greater number are slightly high. The results with metallic aluminium were still higher. We suspected the cause to be alkali in the precipitates, an impurity which our method of washing had not sufficed to remove. Taken as a whole, however, the results appeared sufficiently encouraging to justify a further study of the method.

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[1] See page 295.

The Completeness of Precipitation.

As previously stated, our preliminary experiments showed that the filtrates from the precipitates by carbonic acid, when they were boiled with hydrochloric acid and then treated with ammonia and ammonium sulphide, yielded not the slightest precipitate. We now subjected the filtrates to a more rigid test, by evaporating the same to dryness with pure hydrochloric acid in a platinum basin, taking up the residue in a little boiling water, precipitating with ammonia, filtering, washing thoroughly, igniting in a tared platinum crucible, and weighing the insoluble residue. The results are given below:

Filtrate.		Gram.
1	Precipitate by ammonia, less ash	0.00021
2	“ “ “ “ “	0.00051
3	“ “ “ “ “	0.00061
	Average,	0.00044

Each of these filtrates had a volume of about 0.5 liter. Now, the average of three determinations showed us that our distilled water contained 0.00046 gram residue per 0.5 liter, a portion of which, in the above-mentioned operation, would appear as "insoluble" residue. We therefore conclude that not only is the alumina completely precipitated but also the impurities in the potash; *viz.*, iron, alumina, and silica.

Solubility of the Basic Carbonate of Aluminium.

This was determined by preparing some of the substance as in an ordinary analytical determination, washing thoroughly with cold water, shaking up with distilled water, and allowing it to stand for a week or more at nearly constant temperature, filtering out 1 liter of the solution into a dry measuring flask, evaporating to dryness in a platinum basin, and finally ransferring to, and evaporating in a weighed platinum crucible. A blank with distilled water was carried out under the same conditions. To guard against imperfect washing, the process was repeated with the same material until the results were constant :

		Gram.
1st det.	1 liter of solution at 20° C. contained	0.0025
	Blank	0.0011
		0.0014
2nd det.	1 liter of solution at 20° C. contained	0.0025
	Blank	0.0012
		0.0013

This substance is not a perfectly pure compound, as the sequel shows. Besides, when heated to redness it loses about 5 per cent of carbon dioxide. The above results, therefore, have no value as determinations of a physical constant, but they suffice to show that even in pure water the substance is practically insoluble—much less soluble, for example, than barium sulphate.

Composition of the Precipitate.

The precipitate which carbon dioxide throws down from a soluble aluminate has generally been assumed to be crystalline hydroxide, though Day[1] has shown it to be a basic carbonate. He prepared and analyzed a large number of preparations, but his conditions varied from ours in that his aluminate solutions must have contained an excess of alkali. He found that the substance always contained carbon dioxide and alkali though the percentages varied widely. We find that when potash is added to an aluminium solution, in quantity just sufficient to redissolve the precipitate which first forms, carbon dioxide acts on the aluminate with the formation of an insoluble substance of nearly constant composition. The following preparations were precipitated from solutions of various concentrations (1 gram Al_2O_3 : 1500 cc. H_2O to 1 gram Al_2O_3 : 3000 cc. H_2O), washed with cold water and air-dried.

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[1] This JOURNAL, **19**, 707 (1897).

Analyses of Basic Carbonate of Aluminium.

I. 0.2144 gram substance gave 0.1092 gram Al_2O_3 and 0.0027 gram K_2SO_4.
0.3813 gram substance lost 0.1825 gram on ignition.
0.8480 gram substance gave 0.3503 gram H_2O and 0.0438 gram CO_2.
II. 0.7440 gram substance gave 0.3144 gram H_2O and 0.043 gram CO_2.
III. 0.1996 gram substance gave 0.09975 gram Al_2O_3.
IV. 0.5802 gram substance lost, on ignition, 0.2882 gram.
0.5707 gram substance gave 0.2388 gram H_2O and 0.0267 gram CO_2.
0.3900 gram substance gave 0.1960 gram Al_2O_3 and 0.0026 gram K_2SO_4.
V. 0.1995 gram substance gave 0.09954 gram Al_2O_3.

	Calculated for $4Al_2O_3.CO_2.20H_2O$ or $Al(OH)CO_3.7Al(OH)_3.9H_2O$.			Found.		
		I.	II.	III.	IV.	V.
H_2O	44.29	41.31[1]	42.26[1]	....	41.84[1]	....
CO_2	5.41	5.17	5.78	....	4.68	....
Loss on ignition	49.70	47.87	....	....	49.68	....
Al_2O_3	50.30	50.94	....	49.98	50.26	49.90
K_2O	....	0.68	....	....	0.36	....

The water and carbon dioxide were determined by heating the substance in a hard glass tube as high as possible and collecting in sulphuric acid and caustic potash, respectively. The alumina was carefully precipitated from a hydrochloric acid solution of the substance by means of ammonia. The filtrate was then evaporated in platinum and the residue treated with water and a little ammonia to recover traces of alumina, after which the second filtrate was again carried to dryness, also in platinum. The residue was then transferred to a large platinum crucible, from which the ammonium salts were driven at a low red heat. The residue was now treated with a few drops of pure sulphuric acid, and heated to redness again. Finally, to guard against the formation of acid sulphate, the residue was heated a third time with pure ammonium carbonate. From the weight of the potassium sulphate thus obtained, the residue obtained in a blank was subtracted. The quantity of potash is evidently too small to be regarded as an essential constituent. A small quantity of carbonate or acid carbonate is probably held in the substance by capillary attraction. The experiments of Day show that this compound possesses an unusual capacity for absorption. If we consider the reduction of percentages produced by the impurity and also the error to which the water determinations were subject, the numbers are seen to agree well with a fairly simple formula, *viz.*, $Al(OH)CO_3.7Al(OH)_3.9H_2O$.

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[1] The results for water are probably all low except perhaps in I. We had no platinum tube at our disposal, and we did not succeed in getting a sufficient temperature, using a glass tube.

Decomposition of the Basic Carbonate of Aluminium by Water.

We found that when the carbonate was treated with boiling water it underwent a decided change in appearance, becoming flaky and apparently amorphous. This change of state marks a change in composition, the basic carbonate loses carbon dioxide, water, and alkali, and becomes the hydroxide, $Al(OH)_3$. The gas evolved in the decomposition carries the flakes of the precipitate to the top of the liquid and for a time prevents rapid settling. The following are analyses of preparations boiled with six and eight successive portions of water, respectively, and air-dried:

I. Boiled with water six times:

0.3461 gram substance gave 0.2284 gram Al_2O_3 and 0.0023 gram K_2SO_4.

0.3353 gram substance lost, on ignition, 0.1146 gram.

	Calculated for $Al(OH)_3$.	Found.
Al_2O_3	65.43	65.99
H_2O	34.57	34.18
K_2O	0.00	0.36
		100.53

II. Boiled with water eight times:

0.2393 gram substance gave 0.1571 gram Al_2O_3 and no K_2SO_4.

0.4755 gram substance lost, on ignition, 0.1642 gram H_2O.

	Calculated for $Al(OH)_3$.	Found.
Al_2O_3	65.43	65.65
H_2O	34.57	34.53
K_2O	0.00	0.00
		100.18

It seemed altogether probable that the alkali might be removed more rapidly by boiling the preparation with water containing a little chloride or nitrate of ammonium. This we found to be the case.

III. Basic carbonate of aluminium, after boiling with three successive portions of water containing a little ammonium nitrate. Air-dried.

0.5292 gram substance lost, on ignition, 0.1810 gram.

0.3454 gram substance gave 0.2292 gram Al_2O_3 and no K_2SO_4.

	Calculated for $Al(OH)_3$.	Found.
Al_2O_3	65.43	66.36
H_2O	34.57	34.20
K_2O	0.00	0.00
		100.56

In our first determinations we avoided boiling the precipitate, and sought for conditions under which the alkali could be removed without changing its dense character.

Our results showed that this could be done with ammonium alum. The higher results which we obtained with other substances were probably due in part to the absence of ammonium salts, which, in case of the alum, decomposed the potassium carbonate retained by the precipitate during the washing with hot water, thus:

$$2KHCO_3 + (NH_4)_2SO_4 = K_2SO_4 + 2CO_2 + 2NH_3 + 2H_2O.$$

The potassium sulphate formed is more readily removed.

Properties of Aluminium Hydroxide Formed from the Basic Carbonate.

Fortunately, we found the hydroxide formed in this way much denser than the ordinary variety. It still filtered rapidly and was so compact that we found no difficulty in washing 0.350 gram on a 9 cm. filter-paper. The precipitate does not always settle well after it has been boiled several times with water, but it still washes rapidly with the aid of the pump. The addition of the ammonium salt not only removes the alkali as explained above, but it prevents the solution of alumina to which this variety of hydroxide is as liable as any other. Finally, though we wash on the filter with pure water, we have proved by experiment that, even when a considerable quantity of ammonium chloride remains in the precipitate, the weight of alumina which is volatilized on ignition is almost inappreciable. Theoretically, ammonium nitrate should be better than ammonium chloride, and practically, both work well.

Ignition.—Aluminium hydroxide, as is well known, requires the highest heat of the blast-lamp for complete dehydration. Handy[1] states that the resulting oxide is very hygroscopic. Our results accord with his. As such substances sometimes become denser and less hygroscopic at higher temperatures, and as Fresenius and other authorities on quantitative analysis do not mention this property of aluminic oxide, we concluded to try the effects of a higher heat. Platinum crucibles containing precipitates which had been heated for ten minutes in the blast-lamp, were set on an unglazed porcelain tile inside the muffle of a Hoskin's gasoline furnace. The maximum temperature reached was 1150° C. as measured by the electromotive force of a platinum-rhodium couple. The precipitates were kept for half an hour at this temperature, but after cooling they were as hygroscopic as ever.

Weighing.— All crucibles were heated in a blast-lamp and cooled for from ten to fifteen minutes in a sulphuric acid desiccator. The weight was then taken quickly, after which the crucible was again heated and cooled as before. The weights were now placed in the pan and the rider in the position it occupied during the first weighing. Then the crucible was quickly placed in the other pan and its weight estimated from the first swing of the beam. The weight of the crucible with the precipitate was taken under exactly the same conditions as that of the empty crucible. We employed a set of weights which we had carefully corrected.

Results on "C. P." Aluminium.—We first carefully determined the impurities of the metal as follows: The estimation of total silicon was made according to the method given by

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[1] J. Am. Chem. Soc., 18, 768.

Handy.[1] The iron was determined colorimetrically. The standard solution was made from pure ferric chloride. The iron in it was determined by precipitation with ammonia. A carefully weighed quantity of metallic aluminium was then dissolved in pure hydrochloric acid, oxidized by pure chlorine water, and diluted to a measured volume.[2] A measured volume of the solution was then run into a Nessler cylinder, diluted to 50 cc. and treated with 2 cc. of a 10 per cent solution of potassium sulphocyanate. The tint it gave was matched by that of a measured volume of the standard under the same conditions.

Metal I. 1.0403 grams substance gave 0.0083 gram SiO_2.
1.0037 grams dissolved in HCl was diluted to 250 cc.
10 cc. of this solution matched the tint given by 1.2 cc. standard. 1 cc. standard contained 0.0313 mg. Fe.

Metal II. 1.1878 grams substance gave 0.0142 gram SiO_2.
1.0009 grams were dissolved, oxidized, and diluted to 500 cc. 5 cc. of this solution = 1.4 cc. standard.

	I.	II.
Si	0.37	0.56
Fe	0.094	0.44
Al (diff.)	99.536	99.00

A consideration of the methods used, as well as a careful repetition of our analyses, convinced us that our results were correct within a few hundredths of 1 per cent. As silicon and iron were the only impurities found, we subtracted the sum of these from 100 per cent and called the difference aluminium. Standard solutions of these two samples were prepared by dissolving known weights in pure hydrochloric acid and oxidizing with pure chlorine. When the excess had been boiled out the solutions were very carefully filtered from the finely divided silicon and diluted to 500 cc.

The concentrations of these are given below:

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[1] J. Am. Chem. Soc., **18**, 768.

[2] We observed that the very dilute solution of ferric chloride, which at first showed no trace of ferrous iron, became reduced on standing. The addition of chlorine water does not interfere with the sulphocyanate test.

Solution A. 1.0023 grams metal I in 500 cc.
" B. 1.0009 " " II " " "
" C. 1.0089 " " III " " "

The determinations of aluminium in these solutions were carried out as previously explained. 50 cc. were used for each. The table which follows for the most part explains itself. In the column under "calculated" are found the numbers calculated from the percentages of iron, and the percentages of aluminium obtained by difference:

Volume taken. cc.	Solution.	KOH used.	Imp. in KOH + filter ash.	Weight of precipitate found.	$Al_2O_3 + Fe_2O_3$ found.	$Al_2O_3 + Fe_2O_3$ calculated.	Difference.
50	A	1.563	0.00104	0.18939	0.18835	0.18825	+0.10
50	A	1.697	0.00111	0.18953	0.18842	0.18825	+0.17
50	B	1.653	0.00109	0.18853	0.18744	0.18747	—0.03
50	B	1.630	0.00107	0.18808	0.18701	0.18747	—0.46
50	B	1.630	0.00107	0.18853	0.18746	0.18747	—0.01
50	B	1.530	0.00101	0.18780	0.18679	0.18747	—0.68
50	A	1.848	0.00146	0.19033	0.18887	0.18825	+0.62
50	A	1.993	0.00152	0.19028	0.18876	0.18825	+0.51
50	B	2.022	0.00155	0.18959	0.18804	0.18747	+0.57
50	B	2.022	0.00155	0.18910	0.18755	0.18747	+0.08
50	C	1.930	0.00132	0.19048	0.18916	0.18897	+0.19
50	C	1.930	0.00132	0.19078	0.18946	0.18897	+0.49
						Average,	+0.13

Detailed Directions for the Method.

Dissolve the substance in which the aluminium is to be determined in water or a mineral acid. In case the latter is used, nearly neutralize with ammonia. Now dissolve a stick of potash in which the silica, iron, and alumina are known, in a measured quantity of water, and mix thoroughly. 1–2 grams of potash should be sufficient. Pour the potash solution into a burette, and from thence introduce into the aluminium solution a quantity of the former, sufficient to redissolve the precipitate which first forms. If the solution is still turbid no harm is done, but any considerable excess of potash should be avoided. We have also used soda and, so far as our experience goes, it may be used as well as potash. Now pass a stream of carbon dioxide into the solution. If the alkali is not in too great excess, precipitation begins in a minute or two. Twenty minutes should suffice to precipitate 0.200 gram Al_2O_3. In testing the method we usually allowed the precipitate to settle completely or nearly so, but the bulk of the alumina comes down in a few minutes, and filtration then proceeds without difficulty. Transfer the precipitate for the most part to a 9 cm. filter and wash several times without suction. The soluble impurities are now mostly removed. Break the paper with a stirring rod, wash back completely into the original beaker, and boil the precipitate a few minutes with about 150–200 cc. water containing a little pure ammonium chloride or nitrate. The boiling should be continued only two or three minutes, otherwise the precipitate does not settle well. As soon as it has settled, pass the supernatant liquid through a new filter, using this time a pump and cone. Repeat the boiling and decantation once or twice, transfer the precipitate to the filter, and wash several times with hot water. Suck dry and transfer to a covered crucible, which has been weighed as directed previously. Dry carefully over the flame, burn the paper,[1] and heat from five to ten minutes at the highest temperature of the blast-lamp. Cool from ten to fifteen minutes in a sulphuric acid desiccator, and make an approximate weighing. Heat again for five minutes, cool as before, and weigh as directed. From the weight of the precipitate subtract the weight of the impurities in the potash.[2]

Summary.

1. The precipitate which carbonic acid throws down from sodium or potassium aluminate is a basic carbonate of aluminium containing small amounts of alkaline carbonate. The latter may be effectually removed by boiling with water containing a little ammonium chloride or nitrate. At the same time the precipitate changes to the hydroxide, $Al(OH)_3$. The

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[1] Of course this means both filters.

[2] In technical work where the greatest accuracy is not required, one may easily omit weighing the potash after a little experience. Generally the impurities amount to about 0.001 gram in C. P. potash.

silica, iron, and alumina in the alkali come down with the precipitate.

2. We find the aluminium hydroxide prepared as above is dense and filters rapidly. 0.350 gram can be washed with far less difficulty than 0.050 gram precipitated by ammonia. It is so compact that the above weight may be washed without trouble on a 9 cm. paper.

3. Parallel determinations show that this method is much more rapid than the old one, while the results can be uniformly depended on.

4. It is accurate in the presence of sulphates, while the old method under this condition gives high results.

5. The method is as accurate as the old one for iron and alumina together, and, where the proportion of the latter is large, may be used to advantage. In the presence of the alkaline earths and lithium the method is not applicable. It is especially adapted to the determination of aluminium in samples of the metal, in certain alloys, the alums, hydroxides, etc., substances which give the most trouble in the precipitation by ammonia. If barium is present, of course it may be removed by sulphuric acid, when the alumina may be precipitated in the filtrate after nearly neutralizing with ammonia.

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THE ACTION OF CAUSTIC HYDROXIDES ON ALUMINIUM.

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It is commonly stated in text-books that aluminium dissolves in caustic alkalies with the evolution of hydrogen and the formation of aluminates, but the latter products of the reaction have been little studied. Cavazzi[1] has investigated the action of sodium and potassium hydroxides on aluminium, and concludes that the soluble salts formed belong to the same type as the natural aluminates, *viz.*, $MAlO_2$.

We have further examined these reactions and also the action of lithium, barium, strontium, and calcium hydroxides. These reagents all exert a decided action on the metal even in the cold. The products belong to several different types according to the chemical nature of the hydroxide and the conditions of experiment. The samples of aluminium we used in our work were the so-called " C. P." metal of the market. Their composition follows:

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[1] Gazz. chim. ital., **15**, 202 (1885).

	I.	II.
Al	99.41	99.64 (by diff.)
Fe	0.05	0.02
Si	0.42	0.34
	99.88	100.00

I. Action of Potassium Hydroxide.

A solution of 4.5 grams of caustic potash in 45 cc. water was poured into a large silver crucible, and to it was added sheet aluminium cut into small pieces. Effervescence began immediately, the temperature rose from the heat evolved, and at 60° C. the reaction was vigorous. After some time and while the action was still strong, a white crystalline precipitate began to separate. This soon formed, on the surface of the metal and on the sides of the vessel, a hard, porcelain-like layer, difficult to remove. A portion of this product was washed with alcohol and dried in the sun.

I. 0.5194 gram substance gave 0.1804 gram H_2O.
0.1597 gram substance gave 0.1053 gram Al_2O_3.

II. 0.4252 gram substance gave 0.1430 gram H_2O.
0.3469 gram substance gave 0.2257 gram Al_2O_3.

	Calculated for $Al(OH)_3$.	Found.	
		I.	II.
H_2O	34.57	34.73	33.64
Al_2O_3	65.43	65.93	65.06

The product was therefore crystalline aluminium hydroxide. To decide whether this was formed through the agency of the carbon dioxide of the air, we repeated the experiment, using a glass flask instead of the crucible. The reaction mixture was protected from the air by a stream of hydrogen which had been previously washed by caustic soda. The result was the same. The hydroxide was therefore due to the action of water on the dissolved aluminate.

Cavazzi[1] states that the alkalies dissolve aluminium in the proportion demanded by the equation :

$$2MOH + 2Al + 2H_2O = 2MAlO_2 + 3H_2.$$

We repeated his experiments, using 4.5 grams of potash in 45 cc. water. The reaction did not appear to slacken until hydrolysis set in, when the surface of the metal became rapidly coated with aluminium hydroxide. On the addition of fresh metal the reaction progressed vigorously, and was so continued until we were satisfied that as long as the water was replenished and a fresh metallic surface exposed, aluminium would continue to evolve hydrogen and form hydroxide. At the end of the experiment the pieces of metal which remained were cleaned, dried, and weighed. 6.9 grams had been consumed, whereas, 4.5 grams of potash, according to Cavazzi, should dissolve 2.17 grams metal.

Cavazzi appears to have used a more dilute solution than the above (1 gram KOH : 20 cc. H_2O), but mentions no decomposition. He considered the equivalency of aluminium and potash an argument for the composition of the product. He also evaporated the solution of the metal to dryness, obtaining a gummy mass which contained for 39.1 parts of potassium, 26.55 parts of aluminium.

Potassium Aluminate, $K_2Al_2O_4.3H_2O$.—In accord with the principle of mass action, hydrolysis of the aluminate does not take place when the potash is in considerable excess. Seven grams potash in 70 cc. water was used to dissolve 2.25 grams metal. The solution was filtered from silicon and set away in a vacuum desiccator over sulphuric acid. When the liquid had become quite syrupy, hard, wart-like, crystalline aggregates appeared. The microscope showed them to consist of transparent tables. They were separated from the solution mechanically, washed, and then repeatedly ground in a mortar with alcohol which had been distilled over lime. The snow-white crystalline powder was then dried over sulphuric acid *in vacuo*.

0.4155 gram substance gave 0.0907 gram H_2O.
0.2199 gram substance gave 0.0885 gram Al_2O_3.

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[1] Gazz. chim. ital.. **15**, 202.

	Calculated for $K_2Al_2O_4.3H_2O$.	Found.
K_2O (diff.)	37.63	37.93
H_2O	21.56	21.82
Al_2O_3	40.80	40.25

Potassium aluminate is insoluble in alcohol, soluble in water only with partial decomposition into free potash and amorphous aluminium hydroxide, even when an extremely small quantity of solvent is used. It is hygroscopic and sensitive to carbonic acid. The same substance was long ago obtained by Fremy[1] by dissolving alumina in potash. We are able to verify all his statements concerning it except its complete solubility in water.

In the reaction between potash and aluminium, an excess of the latter makes no difference except that a certain quantity is, of course, necessary to effect hydrolysis, but no acid salt was obtained. By the use of a large excess of potash an attempt was made to isolate a derivative of the normal aluminium hydroxide, but without success. 1.12 grams metal were dissolved in 7 grams potash and 50 cc. water. The ratio 3KOH : Al demands 6.96 grams potash for 1.12 grams metal. After the solution had evaporated for several days *in vacuo*, both its upper and lower surfaces were found encrusted with crystals. Alcohol did not change their appearance.

0.4329 gram substance gave 0.0949 gram H_2O.

	Calculated for $K_2Al_2O_4.3H_2O$.	Found.
H_2O	21.56	21.92

II. Action of Sodium Hydroxide.

Sodium hydroxide exerts on aluminium an action analogous to that of potash. It is decided at ordinary temperatures, and, as the temperature rises, becomes vigorous or violent according to the strength of the soda solution. But even in strong solutions, when the quantity of metal is that required by the ratio Al : NaOH, hydrolysis invariably takes place. Cavazzi[2] took 1 gram caustic soda in 20 cc. water, dissolved by its aid 0.6775 gram aluminium, evaporated the solution to dryness, and subjected the residue to analysis. He states

[1] Ann. chim. phys. [3], **12**, 362.

[2] Gazz. chim. ital., **15**, 202.

that it contained 23 parts of sodium to 26.11 parts of aluminium. This agrees well with the formula $NaAlO_2$, but in view of the fact that we always observed hydrolysis under such conditions as those above specified, and since sodium aluminate requires a high temperature for dehydration, Cavazzi's preparation must have been, at least in part, the product of several reactions. We, therefore, considered it worth while to attempt the isolation of the aluminate by a process involving no secondary reactions. Sodium aluminate is described by Fremy and Cavazzi as a gummy mass. We could not bring a solution of it to crystallization by evaporation *in vacuo*. In one case we dissolved 2 grams of aluminium in 5 grams caustic soda contained in 50 cc. water. With such an excess of alkali no alumina separates. The filtered solution was evaporated *in vacuo* to a thick colorless syrup. This syrup was spread on a porous tile and then kept *in vacuo* over sulphuric acid and phosphorus pentoxide for some weeks without any sign of crystallization. When the syrup is rubbed in a mortar with successive portions of alcohol it assumes the consistency of candied sugar. If this product is then boiled repeatedly with alcohol it loses water and soda, and on cooling becomes hard. It may now be ground with cold alcohol into a powder and dried in a vacuum desiccator. Most of the free soda is extracted by alcohol without difficulty, but the last portion of 2 or 3 per cent apparently cannot be removed by alcohol which has been distilled over lime. Ninety-five per cent alcohol removes it, but if its action is long continued hydrolysis will take place. The following are analyses of two preparations made by the above method :[1]

I. 0.2040 gram substance gave 0.0601 gram H_2O.
0.1971 gram substance gave 0.0876 gram Al_2O_3.
II. 0.3399 gram substance gave 0.0999 gram H_2O.
0.2992 gram substance gave 0.1249 gram Al_2O_3.

	Calculated for $Na_2Al_2O_4.4H_2O$.	Found. I.	Found. II.
H_2O	30.49	29.46	29.39
Al_2O_3	43.26	44.46	41.75
Na_2O (diff.)	26.25	26.08	28.86

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[1] To avoid the presence of sodium carbonate in the final product, the soda solution used to dissolve the aluminium was boiled with a small lump of lime, and filtered.

I. $Al_2O_3 : Na_2O : H_2O = 1 : 0.967 : 3.763$.
II. $Al_2O_3 : Na_2O : H_2O = 1 : 1.14 : 4.00$.

An attempt was made to isolate the compound Na_3AlO_3. Metallic aluminium was dissolved in the theoretical quantity of caustic soda, but no crystals were obtained from the solution in the vacuum desiccator. Tissier[1] claims to have prepared this compound by the action of lime on cryolite, but it should be noticed that the soluble products of the reaction were calcined at a red heat before analysis.

He obtained from the calcined substance 34.66 per cent alumina instead of 35.46 per cent demanded by Na_3AlO_3. We find no convincing evidence that Na_3AlO_3[2] can be formed in the wet way.

III. Action of Lithium Hydroxide.

Caustic lithia reacts with aluminium quite vigorously. In a comparatively short time a precipitate separates which at first we judged to be aluminium hydroxide but which careful examination proved to be a difficultly soluble aluminate. A number of preparations were made. The following conditions gave good results:

Four grams of lithium hydroxide is dissolved in 75 cc. water, boiled a minute or two with a small lump of pure lime to precipitate carbonate, and quickly filtered into a round-bottomed flask of 250 cc. capacity. Several grams of aluminium in small pieces are now added and the flask stoppered with a rubber stopper provided with a Bunsen valve. As soon as a considerable precipitate has formed it is quickly filtered, washed rapidly several times with cold water, followed by alcohol, and finally ether. It may be dried over calcium chloride or air-dried in the sun, provided it is not too long exposed. The following preparations were made under the same or slightly differing conditions.

I. 0.2047 gram substance gave 0.0944 gram H_2O.
0.1264 gram substance gave 0.0593 gram Al_2O_3.
II. 0.2451 gram substance gave 0.1121 gram H_2O.
0.1768 gram substance gave 0.0835 gram Al_2O_3.

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[1] C. R., **43**, 102.

[2] The statement of Graham-Otto, Vol. IV., Part 1, p. 90, regarding Na_3AlO_3 is evidently an error.

III. 0.2588 gram substance gave 0.1194 gram H_2O.
0.1984 gram substance gave 0.0944 gram Al_2O_3.

	Calculated for $LiH(AlO_2)_2.5H_2O$.	Found.		
		I.	II.	III.
H_2O	45.80	46.11	45.73	46.15
Al_2O_3	47.27	46.91	47.23	47.47
Li_2O (diff.)	6.93	6.98	7.04	6.38

Heated in a stream of pure dry hydrogen, 1.7635 grams at 100° C. lost 0.1399 gram, = 7.94 per cent.

A loss of 1 mol. H_2O from $LiH(AlO_2)_2.5H_2O$ = 8.32 per cent.

1.7884 grams at 200° C. lost 0.6040 gram = 33.78 per cent.

A loss of 4 mols. H_2O from $LiH(AlO_2)_2.5H_2O$ = 33.31 per per cent.

2.3705 grams at 275° C. lost 0.9600 gram = 40.50 per cent.

A loss of 5 mols. H_2O from $LiH(AlO_2)_2.5H_2O$ = 41.62 per cent.

In a vacuum desiccator over sulphuric acid one preparation had not reached equilibrium after several months.

Another preparation, which stood two weeks over sulphuric acid *in vacuo* during hot weather, had the composition $LiH(AlO_2)_2.3H_2O$.

0.1803 gram substance gave 0.0637 gram H_2O.

0.1621 gram substance gave 0.0917 gram Al_2O_3.

	Calculated for $LiH(AlO_2)_2.3H_2O$.	Found.
H_2O	34.96	35.33
Al_2O_3	56.72	56.57

Lithium aluminate is a light, white, coarsely granular substance. Under the microscope it is found to consist of very minute, wart-like clusters of crystals. It is much more stable toward water than the soluble aluminates of potassium and sodium. It may be washed repeatedly with cold water in which it is slightly soluble, but by boiling water it is slowly decomposed, though not greatly changed in appearance. After boiling one hour with successive portions of water, one preparation contained but 2 per cent lithia instead of 6.98 per cent. If, during the preparation of lithium aluminate, the solution is quickly filtered before much precipitation takes place, it solidifies in a few minutes to a voluminous, soapy substance of the same composition as the precipitate. It cannot, however, be again dissolved by heating either with water or a solution of lithium hydroxide, except in very small quantities. Thus we have here a solution which seems to be supersaturated. It will be noticed that this compound belongs to a new type of aluminates, $MH(AlO_2)_2$. We were unable to obtain any other aluminate of lithium.

III. Action of Barium Hydroxide.[1]

A hot concentrated solution of this base was first tried. Its action is vigorous in the beginning, but soon slackens, owing to the formation of a protective layer of aluminate on the surface of the metal. 30 to 40 grams of crystallized barium hydroxide was dissolved in 75 cc. hot water and filtered into a 250 cc. flask. The aluminium in small strips was now added and the flask was closed by a stopper with a Bunsen valve. A low flame kept the contents of the flask near the boiling-point. More metal was introduced from time to time until enough of the product for examination had formed. Most of it adhered tenaciously to the glass and metal. It was decidedly heavy, coarsely crystalline, somewhat soluble in water and decomposed by it. Under the microscope, comparatively large, transparent, monoclinic tables were observed. We found it so unstable as to require rapid and careful washing. Several preparations were largely decomposed by too long contact with water. The excess of baryta may be removed by washing rapidly two or three times with cold water, using the pump. The crystals should then be washed with alcohol and dried a short time over sulphuric acid.

I. 0.4373 gram substance gave 0.0790 gram H_2O.
0.2835 gram substance gave 0.2633 gram $BaSO_4$.

II. 0.2059 gram substance gave 0.0353 gram H_2O.
0.2358 gram substance gave 0.2247 gram $BaSO_4$ and 0.0464 gram Al_2O_3.

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[1] Beckmann studied the action of this base on aluminium, but as his metal was quite impure and his solutions were dilute he isolated no product but $Al(OH)_3$. J. prakt. Chem., 26, 392 (1882).

	Calculated for $Ba_2Al_2O_5.5H_2O$.	Found. I.	Found. II.
H_2O	18.04	18.07	17.15
Al_2O_3	20.47	20.89 (diff.)	19.67
BaO	61.48	61.04	62.62

The same compound was obtained by Beckmann by the dissolving alumina in baryta water and crystallizing.[1] His observations agree with ours throughout.

In cold saturated baryta water containing an excess of undissolved crystals, aluminium dissolves rather slowly with the formation of an unstable amorphous(?) salt of a different type.

15 grams crystallized barium hydroxide was dissolved in 70 cc. hot water and filtered into a small Erlenmeyer flask, which was at once stoppered. The contents were then chilled by a jet of cold water, when most of the base crystallized out. The flask was then opened while a few pieces of metal were introduced, and again closed by a stopper with a Bunsen valve. A moderate evolution of hydrogen was observed, but the solution of the metal was comparatively slow. It depends on temperature, but is measured by days rather than hours. The crystals gradually passed into solution as the action proceeded and the product then gradually separated out. The product must be sucked off with the aid of pump and cone, and washed as rapidly as possible in the same way, first with water, then with 50 per cent alcohol, followed by concentrated alcohol. On account of the glutinous nature of the precipitate the operation is at best rather slow, so that the surface must be protected from the atmosphere. We carried out the washing in an apparatus swept by a current of air freed from carbon dioxide.

I. Washed once with cold water, several times with 50 per cent alcohol, and finally with 95 per cent alcohol. Dried a short time over sulphuric acid.

0.5452 gram substance gave 0.1502 gram H_2O.

0.2599 gram substance gave 0.1734 gram $BaSO_4$.

	Calculated for $Ba(AlO_2)_2.5H_2O$.	Found.
H_2O	26.05	27.54
BaO	44.39	43.84
Al_2O_3 (diff.)	29.57	28.62

$Al_2O_3 : BaO : H_2O = 1 : 1.02 : 5.46$.

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[1] J. prakt. Chem., 26, 398.

II. Washed twice with water, several times with 50 per cent alcohol, dried in air free from carbon dioxide, then over calcium chloride for some hours.

0.2387 gram substance gave 0.0645 gram H_2O.
0.2064 gram substance gave 0.1360 gram $BaSO_4$.

	Calculated for $Ba(AlO_2)_2.5H_2O$.	Found.
H_2O	26.05	27.02
BaO	44.39	43.30
Al_2O_3 (diff.)	29.57	29.68

$Al_2O_3 : BaO : H_2O = 1 : 0.972 : 5.17$.

The compound is a soft, white powder, apparently amorphous, easily decomposed by water and by carbonic acid. Beckmann[1] obtained, in a different way, a barium aluminate of the same type containing 6–7 molecules of crystal water. The difference is doubtless due to the conditions of drying. After our experiments with strontia, to be described later, we tried the behavior of a cold saturated solution of baryta containing a very large excess of undissolved crystals, but the action, except that it was more rapid, appeared to be the same.

V. Action of Strontium Hydroxide.

When aluminium is boiled with a strong solution of strontium hydroxide hydrogen is liberated for a moment, after which there seems to be no further action. None of the other caustic hydroxides behaves similarly. When the metal is treated in the cold with a saturated solution of strontia containing an excess of solid crystals, a slight effervescence begins at once and continues. After some days the crystals pass into solution and a granular, sandy precipitate separates out. It is heavy, decidedly crystalline, and colored slightly brownish by the silicon of the metal.

The results of the analysis follow:

0.3269 gram substance gave 0.0659 gram H_2O.
0.2489 gram substance gave 0.0506 gram Al_2O_3.

	Calculated for $Sr_3(AlO_3)_2.6H_2O$.	Found.
H_2O	20.73	20.16
Al_2O_3	19.60	20.33
SrO (diff.)	59.67	59.51

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[1] J. prakt. Chem., **26**, 406.

The same compound is thrown down in pure condition when a solution of potassium aluminate, containing an excess of potash, is poured into a hot solution of strontium chloride or hydroxide. The compound is then pure white, heavy, and more finely granular. These grains, when examined with the microscope, appeared to consist chiefly of dodecahedra. A considerable number of preparations were studied, and in every case these crystals were in the majority. The normal aluminate of strontium is one of the most stable aluminates. In cold water it is sparingly soluble. It may be washed repeatedly by the aid of a pump. On the other hand, samples which were washed by decantation, and remained longer in contact with water, were in large degree decomposed. The compound is stable over sulphuric acid and sensitive to carbonic acid. The following preparation was precipitated from a hot solution of strontium hydroxide, washed rapidly several times with cold water in air free from carbon dioxide, then with alcohol, and finally with ether.

0.4229 gram substance gave 0.0877 gram H_2O.

0.2676 gram substance gave 0.0519 gram Al_2O_3.

	Calculated for $Sr_3(AlO_3)_2.6H_2O$.	Found.
H_2O	20.73	20.74
Al_2O_3	19.60	19.40
SrO (diff.)	59.67	59.86

The action of strontia on aluminium proceeds in two stages. The first stage, which has just been described, is complete when the strontia has passed into solution. In the second stage, the solution gradually becomes milky and a heavy amorphous precipitate forms. At the end of the first stage the solution is filtered from the normal aluminate. When a sufficient quantity of the second compound has separated from the solution it is filtered, washed, and dried. In appearance it closely resembles the aluminate of barium, $Ba(AlO_2)_2.5H_2O$, but we have succeeded in preparing only one sample which was even approximately pure. All other preparations contained too little strontia, a circumstance which could be accounted for by hydrolysis.[1] The substance, being both finely divided and glutinous, is difficult to wash. The preparation, the analysis of which is given below, was made under practically the same conditions as the barium aluminate,

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[1] On account of the previous separation of strontia in the form of $Sr_3(AlO_3)_2$ the concentration of the base is considerably less than the baryta solution during the formation of $Ba(AlO_2)_2$.

$$Ba(AlO_2)_2.5H_2O.$$

0.2329 gram substance gave 0.0629 gram H_2O.
0.2386 gram substance gave 0.0905 gram Al_2O_3.

	Found.
H_2O	27.01
Al_2O_3	37.93
SrO (diff.)	35.06

$SrO : Al_2O_3 : H_2O = 1 : 1.1 : 4.44$.

VI. Action of Calcium Hydroxide.

When aluminium is added to lime-water no action is noted at first, but in a few minutes large bubbles of hydrogen begin to arise and, very slowly, the metal becomes coated with a white, crystalline layer. The reaction continues for many days. A number of preparations were thus made, but the composition of the products varied. This was probably due to the small concentration of lime-water and the opportunity thus afforded for the action of water. To remedy this difficulty and to prevent the formation of carbonate, a liter flask was filled with air free from carbon dioxide, which was then displaced by saturated lime-water. The flask was closed by a stopper with a Bunsen valve. From the stopper was suspended, by a string, a tube 5 cm. long and 2 cm. in diameter, containing several lumps of lime. Thus the water was kept saturated with the hydroxide throughout the experiment. Ten to fifteen grams of sheet aluminium were used in each experiment. After a number of days the liquid was siphoned off, the tube carefully removed, and the metal with its adherent layer washed with cold water, in an atmosphere free from carbon dioxide. It was then dried by alcohol and ether, when the layer of aluminate was scraped off with a knife, care being taken to avoid the separation of any of the unchanged metal. The aluminate was now further washed by the pump with cold water to insure the extraction of all free lime, and then with alcohol and ether.

I. Dried over sulphuric acid some hours.

0.1854 gram substance gave 0.0609 gram H_2O and 0.0614 gram Al_2O_3.

	Calculated for $Ca_2Al_2O_5.6H_2O$.	Found.
H_2O	33.50	32.85
Al_2O_3	31.70	33.12
CaO (diff.)	34.80	34.03

$Al_2O_3 : CaO : H_2O = 1 : 1.88 : 5.63$.

II. Dried over calcium chloride.

Analysis corrected for residue.[1]

0.2951 gram substance gave 0.1120 gram H_2O.

0.2183 gram substance gave 0.0652 gram Al_2O_3.

0.2183 gram contained 0.0038 gram insoluble residue = 1.74 percent; 0.2951 gram contains 0.0052 gram $Al(OH)_3$ containing 0.0018 gram H_2O.

∴ 0.2899 gram aluminate gave 0.1102 gram H_2O.

	Calculated for $Ca_2Al_2O_5.7H_2O$.	Found.
H_2O	37.04	38.01
Al_2O_3	30.04	30.40
CaO (diff.)	32.90	31.59

$Al_2O_3 : CaO : H_2O = 1 : 1.91 : 7.09$.

Calcium aluminate, $Ca_2Al_2O_5.7H_2O$, is a dense, white, crystalline compound, having a pearly luster. Under the microscope transparent, hexagonal plates may sometimes be observed. It is quite difficultly soluble and only slowly acted upon by water.

By precipitation of hot lime-water by potassium aluminate a crystalline precipitate is obtained which, under the microscope, resembles $Sr_3(AlO_3)_2.6H_2O$. Analysis indicated a similar composition.

0.2322 gram substance gave 0.0689 gram H_2O.

0.2152 gram substance gave 0.0546 gram Al_2O_3.

	Calculated for $Ca_3(AlO_3)_2.6H_2O$.	Found.
H_2O	28.56	29.68
Al_2O_3	27.02	25.33
CaO (diff.)	44.43	44.99

$Al_2O_3 : CaO : H_2O = 1 : 3.24 : 6.65$.

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[1] The aluminate dissolves in warm dilute hydrochloric acid, leaving a small quantity of a difficultly soluble white residue, probably crystalline aluminium hydroxide.

The preparation was washed with water, followed by 50 per cent alcohol, and finally by 95 per cent alcohol. It was dried over calcium chloride. It probably contained a little calcium carbonate.

Summary.

1. The well-known aluminates may all, with one exception, be derived from the three hydroxides of aluminium. This exception, the anhydrous lithium aluminate, is not formed directly in the wet way.

$Al(OH)_3$.	$Al_2H_4O_5$.	AlO_2H.[1]	$Al_4H_2O_7$?
$Ba_3(AlO_3)_2$[2]	$Ba_2Al_2O_5$	$Ba(AlO_2)_2$	
$Sr_3(AlO_3)_2$		$Sr(AlO_2)_2$?	
$Ca_3(AlO_3)_2$	$Ca_2Al_2O_5$		
		$K_2(AlO_2)_2$	
		$Na_2(AlO_2)_2$	
		$LiH(AlO_2)_2$	$Li_2Al_4O_7$

2. The alkalies form aluminates belonging to the lowest type, *i. e.*, those into the composition of which the least base enters. The most soluble bases tried in our work form the least stable aluminates. They decompose with water, forming aluminium hydroxide which is crystalline or amorphous, according to the rapidity of the action. Lithium aluminate contains even less base than sodium and potassium aluminates. It is an acid salt, and being difficultly soluble, is quite stable.

The relative proportions of metal, water, and base, in the case of the alkalies, do not influence the type of salt formed, but do condition the decomposition of the salt.

3. The type of aluminate which the alkaline earths form, varies according to the conditions just mentioned. In the heat we obtained $Ba_2Al_2O_5$, while in the cold we could only obtain $Ba(AlO_2)_2$, even with the greatest excess of base. This was doubtless because only the portion in solution is active in the reaction, and that is greatly increased by the rise in temperature.

$Sr_3(AlO_3)_2$ is obtained where the strontia is in sufficient excess, $Sr(AlO_2)_2$(?) where the active mass is smaller.

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[1] To this list should be added the aluminates of the spinel group, *viz.*, $Be(AlO_2)_2$, $Mg(AlO_2)_2$, etc.

[2] Obtained by Beckmann: J. prakt. Chem. (N. F.), **26**, 413.

Lime-water forms with metallic aluminium, $Ca_2Al_2O_5$. From hot lime-water, $Ca_3(AlO_3)_2$ may be precipitated.

Taking the three alkaline earths together, we may say that the most soluble is least inclined to form aluminates of the highest type. As regards stability, it is unsafe to make comparisons because some are crystalline and some are amorphous, and the state of division of any solid conditions the rate of its chemical action. Thus the difference in the stability of $Sr_3(AlO_3)_2$ and $Sr(AlO_2)_2$(?) is probably due to physical differences, for we should expect the former to be less stable than the latter, judging by its composition.

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THE ACTION OF ALKALINE HYDROXIDES, OF WATER, AND OF HYDROGEN PEROXIDE UPON NITROGEN IODIDE.

BY F. D. CHATTAWAY AND K. J. P. ORTON.

Solutions of alkaline hydroxides rapidly decompose nitrogen iodide; the solid particles quickly disappear, bubbles of nitrogen are evolved even when light is excluded, and a pale yellow liquid is produced containing ammonia, together with hypoiodite, iodate, and iodide of the base.

These facts were known to the chemists who first investigated the compound in Gay Lussac's laboratory. Gay Lussac himself, in his great paper on iodine,[1] states that when nitrogen iodide is placed in a solution of caustic potash it immediately disengages nitrogen and forms the same products as the element. These observations have been confirmed by all who have studied the reaction.

A partial explanation of it has recently been offered by Seliwanow, who regards it as a simple hydrolysis. He endeavored to establish his views experimentally, but was never able to reach more than approximate results.[2]

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[1] Ann. Chim., **88**, 304 (1813).

[2] Seliwanow (Ber. d. chem. Ges., **27**, 102 (1894)), from his study of iodyl succinimide, recognized that compounds containing iodine attached to nitrogen should yield, on hydrolysis, hypoiodous acid or hypoiodites, or the products of their transformation. He treated nitrogen iodide with very dilute sulphuric or acetic acid and estimated the amount of iodine liberated and the amount of iodic acid remaining after

In continuation of our work upon pure nitrogen iodide we have investigated the action of alkalies and of water upon it, and have been able to prove that two reactions invariably occur simultaneously, the extent to which each takes place depending upon the conditions under which the decomposition is effected.

The chief action is one of hydrolysis, ammonia and an alkaline hypoiodite being produced. These hypoiodites, however, are unstable, and more or less rapidly change into iodide and iodate. The equations representing the action of potassium hydroxide, for example, are :

$$N_2H_3I_3 + 3KOH = 2NH_3 + 3KOI = 2NH_3 + 2KI + KIO_3.$$

At the same time a portion of the nitrogen iodide always breaks down exactly as under the influence of light yielding nitrogen or hydrogen iodide, which latter then reacts with some of the alkaline hydroxide, forming an iodide.

For example, with potassium hydroxide, the reactions are :

$$N_2H_3I_3 = N_2 + 3HI ;$$
$$N_2 + 3HI + 3KOH = N_2 + 3KI + 3H_2O.$$

Solutions of ammonium hydroxide and of hydroxides of the alkaline earth metals act similarly.

Water also causes analogous decompositions, but in this case some of the hypoiodous acid formed in the hydrolysis reacts with the hydrogen iodide produced in the simple decomposition, liberating iodine, while any excess becomes itself transformed into iodine and iodic acid :

$$N_2H_3I_3 + 3H_2O = 2NH_3 + 3HOI ; \text{ and } N_2H_3I_3 = N_2 + 3HI ;$$
$$HOI + HI = I_2 + H_2O ;$$
$$\text{and } 15HOI = 10HI + 5HIO_3 = 6I_2 + 3HIO_3 + 6H_2O.$$

These reactions fully explain the production of iodine when

this had been removed. The iodine and iodic acid should be formed in the proportion of 4 atoms of the former to 1 molecule of the latter :

$$5HOI = I_4 + HIO_3 + 2H_2O.$$

In eight recorded experiments he obtained numbers varying by about 25 per cent (from 4.6 to 3.6 atoms of iodine to 1 molecule of iodic acid). It was, however, impossible for him to obtain better results, since his explanation completely neglects the nitrogen evolved. Further, he did not know the composition of the material he was dealing with, and was thus unable to determine its purity. Indeed, he assumes that three compounds exist, and he gives equations representing the hydrolysis of each.

nitrogen iodide is warmed to 50°–60° C. with water, a method which Stas has employed to prepare pure iodine on a large scale.

The action of water on nitrogen iodide is rendered more rapid by the presence of basic oxides and of salts such as iodides and carbonates, which can combine or react with the hypoiodous and hydriodic acids formed.[1]

Hydrogen peroxide dissolved in a solution of potassium hydroxide rapidly decomposes nitrogen iodide, ammonia, potassium iodide, and a trace of potassium iodate being produced, whilst oxygen, mixed with a little nitrogen, is evolved. The nitrogen iodide may be assumed to react with the potassium hydroxide as if it alone were present, being hydrolyzed to ammonia and potassium hypoiodite, but at the same time breaking down partially into nitrogen and hydrogen iodide. A very small quantity of the hypoiodite is transformed into iodide and iodate, but the greater part reacts with the hydrogen peroxide, liberating oxygen and being converted into iodide, thus:

$$KOI + H_2O_2 = KI + O_2 + H_2O.$$

If a solution of hydrogen peroxide be added to nitrogen iodide, no alkali being present, the water hydrolyzes the compound and similar reactions ensue, whilst iodine is set free by a further action of hydrogen peroxide on the hydrogen iodide remaining uncombined.

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[1] In all reactions with nitrogen iodide where hydrolysis takes place, it is accompanied by a breaking down of the molecule into nitrogen and hydriodic acid, the amount of such decomposition altering with the conditions. A variable amount of hydriodic acid or iodine in excess of that corresponding with the decomposition of hypoiodous acid and more approximately to that which would be needed by the action of a periodide is, therefore, always formed. In a paper by one of us (Chattaway: Trans. Chem. Soc., 1896, 1572) attention was drawn to these variable results, and it was suggested that nitrogen iodide might be a periodide, and since, on analysis, the loss of nitrogen lowered the relative proportion of nitrogen to iodine, that it might have the formula NH_3I_2. This formula did account for the analytical results and grouped known facts better than any other could, assuming a single action in each case to take place. The composition of the pure substance has, however, now been established beyond doubt and found to correspond with the formula $N_2H_3I_3$, and it is further here shown that the variability and the excess of hydrogen iodide and iodine always noticed are due to secondary decompositions. The formula NH_3I_2, therefore, is incorrect, and with the above explanation of why it was suggested is unconditionally withdrawn.

Action of Alkaline Hydroxides on Nitrogen Iodide.

Nitrogen iodide, when placed in a strong solution of an alkaline hydroxide, disappears very rapidly, almost instantaneously if the liquid be hot; bubbles of pure nitrogen are evolved, ammonia is liberated, and a pale-yellow solution containing hypoiodite results. The hypoiodite soon becomes transformed into iodide and iodate, and the liquid loses its yellow color and its power of oxidizing arsenites. This change is complete after standing for twenty-four hours in the dark. The alkaline earth hydroxides, the slightly soluble basic oxides, and solutions of ammonia act similarly but more slowly.

The action of caustic potash, being typical, was chosen for careful study. A small quantity of pure crystalline nitrogen iodide was placed in a stoppered flask together with 14 cc. of a 36 per cent solution of potassium hydroxide, and allowed to stand in a perfectly dark, cool cellar at a uniform temperature for forty-eight hours. The nitrogen iodide was thus completely decomposed and all the hypoiodite converted into iodide and iodate.

The ammonia formed was first distilled off into standard acid and estimated. The solution was then made slightly acid with sulphuric acid and the liberated iodine titrated with sodium sulphite. This gives the iodate and consequently the hypoiodite originally produced. The total iodine in the product from the sulphite titration, and hence the quantity of nitrogen iodide used, was finally determined by silver nitrate.

Knowing the amounts of hypoiodite and ammonia produced, these can be compared and the hydrolysis quantitatively followed, while, since the total iodine contained in the nitrogen iodide is given by the silver nitrate titre, the percentage which undergoes decomposition into nitrogen and hydrogen iodide can be calculated.

$\frac{N}{10}$ NH$_3$ obtained by hydrolysis of portion of nitrogen iodide.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$.	$\frac{N}{10}$ AgNO$_3$ = the total iodine in nitrogen iodide in cubic centimeters of a decinormal solution.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ KOI actually produced by hydrolysis of portion of nitrogen iodide.	Amount of potassium hypoiodite in cubic centimeters of $\frac{N}{10}$ KOI that should be produced, calculated from amount of ammonia obtained.	Ratio between NH$_3$ and KOI actually obtained.	Perc'ntage of total nitrogen iodide used that decomposed into nitrogen and HI in the reaction.
cc.	cc.	cc.	cc.	cc.		
16.4	48.9	31.8	24.45	24.6	2.01 : 3	23.1
17.1	51.4	31.1	25.7	25.65	1.99 : 3	17.3
17.5	52.6	32.6	26.3	26.25	1.99 : 3	19.3
20.5	61.5	35.25	30.75	30.75	2 : 3	14.1

The agreement between the amount of hypoiodite estimated (column 4) and that calculated from the ammonia (column 5) is seen to be very close, although the second decomposition (column 7) has taken place to very different extents.

Experiments were next made in a similar manner, but instead of the hypoiodite being allowed to decompose into iodide and iodate before estimation, the yellow solution itself was analyzed, both the hypoiodite and iodate being determined. A quantity of crystalline nitrogen iodide was placed in from 15–20 cc. of a 28 per cent solution of potash and allowed to stand from thirty to sixty minutes in complete darkness. In this time the nitrogen iodide entirely decomposed, but a portion only of the hypoiodite was transformed into iodide and iodate. The hypoiodite was then estimated by arsenite, the iodate afterwards by sulphite, and finally the ammonia by distillation.

$\frac{N}{10}\left(\frac{Na_3AsO_3}{2}\right)$ required to react with potassium hypoiodite form'd	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ required to react with iodine liberated by the iodate.	$\frac{N}{10}$ NH_3 produced in distillation.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_3AsO_3}{2}\right) = \frac{N}{10}$ KOI actually present = *a*.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ KOI equivalent to iodate produced = *b*.	$\frac{N}{10}$ KOI actually produced by hydrolysis of portion of the nitrogen iodide = $a + b$.	$\frac{N}{10}$ KOI that should be obtained calculated from the amount of ammonia produced.	Ratio between NH_3 and KOI obtained.
cc.	cc.	cc.	cc.	cc.	cc.	cc.	
51.2	13.6	21.5	25.6	6.8	32.4	32.25	1.99 : 3
39.2	38.0	25.8	19.6	19	38.6	38.7	2 : 3
19.6	50.6	23.4	9.8	25.3	35.1	35.1	2 : 3

If nitrogen iodide be gradually added to a hot solution of caustic potash, light being entirely excluded, decomposition into nitrogen and hydriodic acid takes place to a very small extent only, almost all of the compound being hydrolyzed; ammonia is given off, and the conversion of the hypoiodite into iodide and iodate is rapid and complete. In order to investigate the action, about 0.5 gram of crystalline nitrogen iodide was added to 10 cc. of a 36 per cent solution of warm caustic potash, and the liquid rapidly heated to 100° and boiled for ten minutes. It was then cooled and acidified with sulphuric acid, after which the iodine liberated by the iodate was estimated by sodium sulphite. The total iodine present was finally determined by distillation with sulphuric acid and iron alum.

If the whole of the nitrogen iodide were hydrolyzed, the ratio of iodine as iodate to total iodine should be as 1 : 3, since

$$3KOI = KIO_3 + 2KI.$$

The ratio, however, is never quite reached, since some of the nitrogen iodide always decomposes into nitrogen and hydriodic acid, but the amount of this change, although variable, is not so large as when the substance is decomposed by cold potash. The conditions of the experiment affect the extent to which each change goes on.

In experiments 1–3, where the nitrogen iodide was added to a solution of potassium hydroxide heated to 60°, from 3–4 per cent only broke down into nitrogen and hydriodic acid, and in experiment 4, where it was added to a similar solution of potassium hydroxide already boiling 11.18 per cent, while, when allowed to decompose in potash of a similar strength at the ordinary temperature (see table, page 322), from 14–23 per cent so reacted.

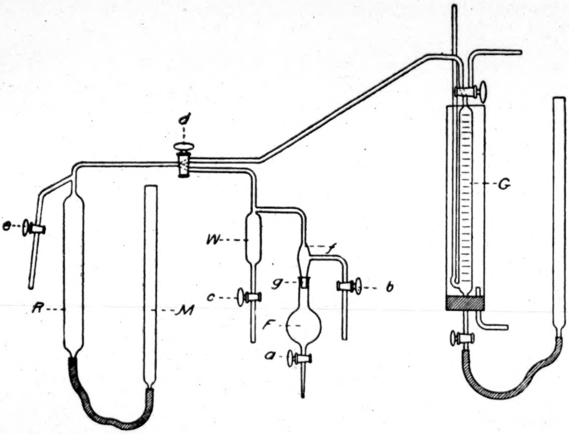
Number of experiment.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ required to react with iodine liberated by iodic acid produced. cc.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ required to react with iodine liberated by distillation with sulphuric acid and iron alum = total iodine as cubic centimeters of a decinormal solution. cc.	$\frac{N}{10}$ I as KIO_3 in product = one-sixth of sulphite titre. cc.	Ratio between iodine as iodate and total iodine in the product calculated as $x : 3$.	Percentage of nitrogen iodide decomposed into hydriodic acid and nitrogen in the experiment.
1	32.2	16.7	5.36	0.962 : 3	3.59
2	32.1	16.6	5.35	0.966 : 3	3.31
3	35.8	18.5	5.96	0.966 : 3	3.24
4	85.8	48.3	14.3	0.888 : 3	11.18

In order to complete the proof that two actions go on simultaneously when nitrogen iodide is decomposed by caustic potash, it is necessary to estimate the nitrogen evolved and to show that this corresponds with the amount calculated from the observed loss of ammonia.

In the following experiments, therefore, the decomposition of nitrogen iodide was effected in a specially constructed piece of apparatus which enabled small quantities of gas to be accurately measured while the liquid was not allowed to come into contact with mercury. Pure crystalline nitrogen iodide was used. It was decomposed by an excess of a 30 per cent solution of potassium hydroxide. The nitrogen evolved was measured and the alkaline liquid distilled, and the ammonia formed estimated. In the residue, after distillation, the iodate was determined by standard sodium sulphite after acidification with sulphuric acid, and finally the total iodine was estimated by distillation with sulphuric acid and iron alum.

Two estimations were made, and in each case the agreement between the actual (column 4) and calculated results (columns 6 and 8) is so close as to put beyond question the correctness of the explanation given :

$\frac{N}{10}$ NH_3. cc.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right) = 2b$. cc.	$\frac{N}{10}$ I contained in nitrogen iodide used $= a$. cc.	Nitrogen evolved in cubic centimeters at 0° and 760 mm. cc.	$\frac{N}{10}$ KOI lost $= a-b$. cc.	Nitrogen that should have been evolved calculated from total iodine and sulphite titre. cc.	$\frac{N}{10}$ NH_3 lost. cc.	Nitrogen that should have been evolved calculated from total iodine and ammonia obtained. cc.
10.1	30.2	18	2.12	2.9	2.161	1.9	2.128
8.4	25.2	15.1	1.82	2.5	1.866	1.67	1.87



Sodium hydroxide behaves towards nitrogen iodide in every respect as does potassium hydroxide. Ammonium hydroxide also acts similarly, with this exception, that, if nitrogen iodide be heated with a solution of ammonium hydroxide and the resulting solution rapidly cooled before the ammonium hypoiodite, through transformation into iodate, falls below a certain concentration, nitrogen iodide is reformed. The action is in this case reversible and obeys the laws of mass action. The effect of hydroxides of the alkaline earths is much the same except that it is slower, as weaker solutions have to be used.

Action of Water on Nitrogen Iodide.

Nitrogen iodide, when allowed to remain suspended in water at the ordinary temperature, light being excluded, slowly decomposes; bubbles of nitrogen are occasionally given off, free iodine is liberated, and ammonium iodide and iodate are formed. The action is very slow, some months being required before a gram or so completely disappears. After standing for some days under water the substance becomes very unstable, the slightest disturbance, even the rising of a bubble of gas, often being sufficient to cause an explosion. If nitrogen iodide be warmed with water to 60°–65°, the decomposition is rapid and explosions do not occur; free iodine separates in quantity, and ammonium iodate and iodide remain in the liquid. This latter mode of decomposition was employed by Stas[1] for preparing pure iodine.

No explanations of these reactions have been brought forward and we have consequently investigated them.

As in most other decompositions of nitrogen iodide, two reactions go on simultaneously, a simple hydrolysis of the substance resulting in the formation of ammonia and hypoiodous acid, and a breaking down of the compound into nitrogen and hydriodic acid. As the latter decomposition frequently takes place to a slightly greater extent than the former, the hydriodic acid is often produced in sufficient quantity to react with all the hypoiodous acid, so that no iodic acid is found. This, however, is not always the case, as the extent to which these two reactions take place varies with all the conditions of the experiment.

The results given below were obtained as follows: Small quantities of crystalline nitrogen iodide were placed in stoppered bottles of from 500–800 cc. capacity; these were then completely filled with water so as to exclude air, and left undisturbed in a perfectly dark cellar for three months. At the end of that time the nitrogen iodide was found to have completely disappeared, a liquid colored brown by free iodine remaining. The free iodine in this was then estimated by sodium sulphite, the free hydriodic acid next by baryta, and finally the total iodine by silver nitrate. The ammonia present was then determined by distillation into standard acid after the addition of potash :

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[1] Chem. Proport, 137.

$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$. cc.	$\frac{N}{10}\left(\frac{Ba(OH)_2}{2}\right) = \frac{N}{10}$ HI free in titrate = *a*. cc.	$\frac{N}{10}$ $AgNO_3$ = total iodine present in nitrogen iodide used as cubic centimeters of a decinormal solution. cc.	$\frac{N}{10}$ NH_3 obtained by distillation = *b*. cc.	Amount of $\frac{N}{10}$ HOI actually produced in hydrolysis $= \frac{1}{2}\left(\frac{Na_2SO_3}{2}\right) = c$. cc.	Amount of $\frac{N}{10}$ HOI that should be produced calculated from ammonia obtained by direct distillation. cc.	Amount of $\frac{N}{10}$ HI produced in reaction obtained by subtracting amount of hypoiodous acid formed from total iodine. cc.	Amount of $\frac{N}{10}$ HI produced in reaction calculated from free iodine produced from amount of free HI present after titration with sulphite given by baryta titre and from ammonia obtained in distillation $= (a+b)-c$. cc.	Percentage of total nitrogen iodide hydrolyzed.	Percentage of total nitrogen iodide decomposed into nitrogen and hydriodic acid.
67.3	52.2	74.7	22.4	33.65	33.6	41.05	40.95	45.1	54.9
53	41.6	59.3	17.5	26.5	26.25	32.8	32.6	44.7	55.3
41.8	35.4	49.3	14	20.9	21	28.4	28.5	42.4	57.6
42.9	35.1	49.4	14.3	21.45	21.45	27.95	27.95	43.5	56.5

The agreement between the amounts of hypoiodous acid actually formed and those calculated from the ammonia produced, and between the amounts of hydriodic acid formed in the reaction calculated from quite different titration numbers proves beyond question that the explanation of the reaction given above is correct.

Nitrogen iodide is decomposed much more readily by a solution of potassium iodide than by pure water, only a few hours being required.

If light be excluded, no nitrogen is evolved, and hydrolysis of the nitrogen iodide only appears to take place, the potassium iodide reacting with the hypoiodous acid and holding the liberated iodine in solution.

In the following experiments nitrogen iodide was treated with an excess of a decinormal solution of potassium iodide, light being completely excluded. After the disappearance of the solid particles, which generally happened in from eight to twelve hours, the resulting liquid was analyzed as follows: It was considerably diluted and the free iodine titrated with sodium sulphite; the free hydriodic acid then present was estimated by baryta, and finally the whole was distilled with potash and the ammonia evolved estimated by standard acid.

The amount of hypoiodous acid corresponding to the free iodine is found, as in all other cases, to agree with that calculated from the ammonia produced, while the fact that no decomposition of the substance into nitrogen and hydriodic acid accompanies this is proved by the circumstance that the amount of the ammonia actually obtained is exactly that which should be produced, calculated from the sulphite and baryta titres.

$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ cc.	$\frac{N}{10}\left(\frac{Ba(OH)_2}{2}\right)$ = free $\frac{N}{10}$ HI. cc.	$\frac{1}{2}\left(\frac{N}{10}\frac{Na_2SO_3}{2}\right)$ — $\frac{N}{10}\left(\frac{Ba(OH)_2}{2}\right) = \frac{N}{10}$ NH_3 that should be produced, assuming that hydrolysis only takes place. cc.	$\frac{N}{10}$ NH_3 actually obtained by distillation with potash. cc.	$\frac{N}{10}$ HIO produced calculated from ammonia actually obtained. cc.	$\frac{N}{10}$ HIO formed = $\frac{1}{2}\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ cc.
45.5	7.5	15.25	15.1	22.65	22.75
55.8	9.3	18.6	18.5	27.75	27.9
48.7	8.1	16.25	16.2	24.3	24.35

The presence of slightly soluble oxides, as, for example, those of magnesium and lead, somewhat accelerates the action of water upon nitrogen iodide, and the acids formed react with them to form iodides and iodates of the metals.

Action of Hydrogen Peroxide upon Nitrogen Iodide.

A solution of hydrogen peroxide alone or in presence of caustic potash, when brought into contact with nitrogen iodide, decomposes it with great rapidity, and oxygen mixed with small quantities of nitrogen is evolved. If hydrogen peroxide alone be used, iodine is liberated and ammonium iodide produced, while, if caustic potash be employed, free ammonia, potassium iodide, and a very small quantity of iodate are formed. A quantity of pure crystalline nitrogen iodide was treated, in the apparatus used in studying the action of potassium hydroxide, with a solution of hydrogen peroxide, and all the products estimated. The gas evolved was analyzed and found to consist only of oxygen mixed with a small proportion of nitrogen. In the liquid product of the reaction, which contained ammonium iodide and free iodine, the ammonia was estimated by distillation into standard acid, and the iodine, after conversion into hydriodic acid by sodium sulphite, was titrated with silver nitrate.

From the amount of ammonia formed, the quantity of nitrogen iodide hydrolyzed can be calculated, and consequently the volume of oxygen that should be obtained by the reaction of the hypoiodite with the hydrogen peroxide. The silver nitrate titre gives the total iodine in the nitrogen iodide used, and the ammonia, the amount hydrolyzed; the quantity, therefore, which has decomposed into nitrogen and hydriodic acid in the reaction, and the volume of nitrogen that should be evolved can be calculated.

The following table gives a comparison of the amounts of oxygen and nitrogen thus calculated with those actually obtained. The numbers given are a mean of two experiments:

$\frac{N}{10}$ $AgNO_3$ = $\frac{N}{10}$ I in the nitrogen iodide used. cc.	$\frac{N}{10}$ NH_3 obtained by distillation. cc.	Amount of oxygen that should be evolved calculated from amount of nitrogen iodide hydrolyzed. cc.	Amount of nitrogen that should be evolved calculated from amount of nitrogen iodide that decomposed into nitrogen and hydriodic acid. cc.	Total amount of gas evolved at 0° and 760 mm. cc.	Total oxygen actually obtained in experiment. cc.	Total nitrogen actually obtained in experiment. cc.
18.00	10.4	34.83	1.79	37.48	36.16	1.32

The results obtained are sufficiently close to show that the explanation given is the correct one, but, as might be expected, the nitrogen is slightly too low, owing to a portion being dissolved in the liquid employed; while the oxygen is somewhat too high, this being due to the fact that hydrogen peroxide itself, under the circumstances of the experiment, slowly gives off oxygen, an action which cannot be prevented or estimated.

In the next experiment the hydrogen peroxide was mixed with caustic potash to prevent the deposition in the apparatus of free iodine which is very difficult to remove completely for purposes of estimation.

Here a portion of the hypoiodite escapes the action of the hydrogen peroxide and becomes converted into iodate. When the ammonia had been distilled off, this was estimated by sodium sulphite after acidification with sulphuric acid. It was allowed for in the calculation by subtracting the amount of hypoiodite equivalent to it from the total amount produced in the hydrolysis. As before, a comparison is made in the table between the amounts of oxygen and nitrogen actually measured and those which should be evolved, calculated from the amounts of nitrogen iodide hydrolyzed and decomposed into nitrogen and hydriodic acid, respectively:

$\frac{N}{10}$ $AgNO_3$. cc.	$\frac{N}{10}$ NH_3. cc.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ required to reduce iodate. cc.	Amount of oxygen that should be evolved. cc.	Amount of nitrogen that should be evolved. cc.	Total amount of gas evolved at 0° and 760 mm. cc.	Total oxygen actually obtained. cc.	Total nitrogen actually obtained. cc.
25.6	14.8	11.6	36.34	2.51	39.89	38.05	1.84

Again, the nitrogen is slightly too low, a little being lost by solution in the liquid, while the oxygen is somewhat high, the excess being produced as before by the spontaneous decomposition of nitrogen peroxide during the experiment.

In the calculations oxygen is taken as 15.84, the weight of 1 cc. of nitrogen as 0.0012507 gram, and that of 1 cc. of oxygen as 0.0014293 gram.

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THE ACTION OF ACIDS UPON NITROGEN IODIDE.

BY F. D. CHATTAWAY AND H. P. STEVENS.

Most chemists who have investigated nitrogen iodide have recorded observations on its behavior towards a few of the commoner acids, so that the ultimate products of such treatment are tolerably well known. The reactions, however, have never been carefully studied nor has any explanation of them been brought forward.

Dilute acids, when added to nitrogen iodide suspended in water, first induce hydrolysis of the compound, and hypoiodous acid is liberated, together with ammonia, which combines with the acid added:

$$N_2H_3I_3 + \text{acid} + 3H_2O = (2NH_3 + \text{acid}) + 3HOI.$$

The further action depends upon the nature of the acid used. If acids be employed such as sulphuric, phosphoric, boric, or acetic, upon which hypoiodous acid has no effect, a rapid change into hydriodic and iodic acids occurs, the former being immediately oxidized by a portion of the latter and iodine liberated:

$$15HOI = 10HI + 5HIO_3 = 6I_2 + 6H_2O + 3HIO_3.$$

If, however, interaction between the acid used and hypoiodous acid is possible, this takes place, and the nature of the final products depends upon the acid employed.

With hydriodic acid, for example, iodine is liberated according to the equation:

$$HOI + HI = I_2 + H_2O.$$

With hydrochloric acid, iodine monochloride is produced:

$$HOI + HCl = ICl + H_2O.$$

While with hydrocyanic acid cyanogen iodide is formed:

$$HOI + HNC = INC + H_2O.$$

In addition to this main action, it is found that, when any acid except hydriodic or hydrocyanic is added to nitrogen iodide, light being excluded, a variable amount, depending on the strength of the acid and all other conditions, decomposes exactly as it does under the influence of light, yielding nitrogen and hydriodic acid; this hydriodic acid then reacts with some of the hypoiodous acid formed in the hydrolysis and liberates iodine.

General Behavior of Nitrogen Iodide towards Acids.

Most acids, if at all concentrated, act very violently upon nitrogen iodide and generally cause explosion. A strong solution of sulphurous acid, even when poured over dry nitrogen iodide, causes it to deteriorate. If, however, the nitrogen iodide be suspended in water, and a solution of acid of about decinormal strength added, rapid, but quiet, decomposition ensues, bubbles of nitrogen generally rise from the decomposing particles which float to the surface, and when the action is over free iodine is, as a rule, found in the liquid.

The actions of hydriodic acid and of hydrocyanic acid are first considered, as these are not complicated by any simultaneous decomposition into nitrogen and hydriodic acid.

Action of Hydriodic Acid upon Nitrogen Iodide.

When a solution of hydriodic acid is added to water containing nitrogen iodide in suspension, the nitrogen iodide is at once decomposed, ammonium iodide is formed, and iodine liberated, no nitrogen being evolved if light be entirely excluded.

In the experiments made to determine the course of the reaction, small quantities of crystalline nitrogen iodide were completely decomposed by the addition of known amounts of a decinormal solution of hydriodic acid. The iodine set free was then estimated by a standard solution of neutral sodium sulphite, whereby it was converted into free hydriodic acid. The amount of free acid in the solution was next estimated by neutralizing the liquid with standard baryta, and finally the total hydriodic acid was determined by standard silver nitrate.

Knowing the amount of hydriodic acid present from the silver titre, if that added to decompose the compound be subtracted, the quantity produced from the nitrogen iodide is obtained. This is found to contain iodine equivalent to half the iodine liberated in the free state; the other half must, therefore, have been obtained from the hydriodic acid added. Thus all the iodine contained in the nitrogen iodide behaves as if it were first liberated as hypoiodous acid.

Also, knowing the total quantity of hydriodic acid present from the silver titre and the amount free from the baryta titre, the ammonia produced which neutralizes the remainder can be calculated. This can also be determined by distilling the final product with caustic potash. Both methods have been adopted. In every case the amount is found to equal that calculated from the free hydriodic acid produced, showing that the nitrogen iodide entirely hydrolyzes into hypoiodous acid and ammonia.

$\frac{N}{10}$ HI added to decompose the nitrogen iodide = *a*. cc.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ = total amount of iodine liberated as cubic centimeters of $\frac{N}{10}$ I. cc.	$\frac{N}{10}\frac{Ba(OH)_2}{2}$ = amount of $\frac{N}{10}$ HI free. cc.	$\frac{N}{10}$ $AgNO_3$ = total amount of $\frac{N}{10}$ HI present after titration with sulphite = *b*. cc.	$b - a = \frac{N}{10}$ HI obtained from nitrogen iodide = $\frac{N}{10}$ I contained in nitrogen iodide. cc.	Half the iodine liberated in free state as $\frac{N}{10}$ I. cc.	$\frac{N}{10}$ NH_3 produced = total amount of $\frac{N}{10}$ HI − amount of $\frac{N}{10}$ HI free. cc.	$\frac{N}{10}$ NH_3 produced estimated by distillation. cc.	$\frac{N}{10}$ NH_3 that should be produced calculated from amount of HI yielded by nitrogen iodide. cc.
31.8	60.1	41.9	61.9	30.1	30.05	20.	. . .	20.06
53.0	83.8	67.0	94.9	41.9	41.9	27.9	. . .	27.93
31.7	40.5	. . .	52.0	20.3	20.25	. . .	13.5	13.53
31.8	46.8	. . .	55.2	23.4	23.4	. . .	15.6	15.6

Action of Hydrocyanic Acid upon Nitrogen Iodide.

Dilute hydrocyanic acid rapidly decomposes nitrogen iodide, and a colorless solution results, containing, if light be entirely excluded, only cyanogen iodide and ammonia. On shaking this solution with ether, the cyanogen iodide is extracted, and crystallizes in white needles on allowing the solvent to evaporate, while the ammonia can be obtained by distilling the residue with potash. Estimations have been made of the amounts of nitrogen iodide required to react with known volumes of a standard solution of hydrocyanic acid, the quantity of the former being determined from the ammonia produced. If the solution of hydrocyanic acid be added to the nitrogen iodide, it is difficult to decompose the last few particles without adding an excess. In the experiments, therefore, it was added to a quantity of nitrogen iodide slightly in excess of the amount required to react with it; the liquid was vigorously shaken for some minutes and the unchanged solid filtered off.[1] The filtrate was then very slightly acidified by sulphuric acid and the cyanogen iodide driven off by rapidly boiling. A little silver nitrate solution was added at the end of the operation to show that the expulsion was complete.

No weighable amount of silver iodide was ever formed, showing that the cyanogen iodide could be expelled thus without hydrolysis, and that no hydriodic acid was produced in the previous reaction. The residue was then made alkaline with caustic potash, and the ammonia distilled off into standard acid. The amount of nitrogen iodide which reacted with the known amount of hydrocyanic acid used can be calculated from this ammonia. In the following results this is shown to be in accord with the equation:

$$N_2H_3I_3 + 3H_2O + 3HNC = 2NH_3 + 3HOI + 3HNC = 2NH_3 + 3INC + 3H_2O.$$

$\frac{N}{10}$ HNC which reacted with nitrogen iodide used. cc.	$\frac{N}{10}$ NH_3 produced in distillation. cc.	$\frac{N}{10}$ I contained in nitrogen iodide used calculated from ammonia produced = $\frac{N}{10}$ HNC required by above equation. cc.
19.7	13.4	20.1
21.7	14.7	22.05

Action of Sulphuric Acid upon Nitrogen Iodide.

Dilute sulphuric acid added in excess to nitrogen iodide suspended in water immediately liberates iodine, while bubbles of nitrogen gas are given off. If the resulting liquid be boiled so as to expel all the free iodine, it is found to contain, besides excess of sulphuric acid, ammonium sulphate and iodic acid. Two reactions here go on simultaneously, a small percentage of the nitrogen iodide breaks up into hydriodic acid and free nitrogen, but the greater part suffers hydrolysis under the influence of the dilute sulphuric acid, producing ammonium sulphate and hypoiodous acid ;[1] a portion of the latter oxidizes the hydriodic acid already formed, liberating iodine, while the remainder undergoes transformation into hydriodic and iodic acids, yielding finally iodine and iodic acid, since the latter, if light be excluded, is always in excess. The following equations represent the changes taking place :

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[1] As a precaution, this nitrogen iodide filtered off was analyzed and found to be unchanged in composition.

$$N_2H_3I_3 = N_2 + 3HI \text{ and } N_2H_3I_3 + 3H_2O + H_2SO_4 = (NH_4)_2SO_4 + 3HOI ;$$

$$15HOI = 10HI + 5HIO_3 = 6I_2 + 3HIO_3.$$

The nitrogen and hydriodic acid formed in the direct decomposition do not prevent an estimation of the ammonia and hypoiodous acid produced in the hydrolysis. Such an estimation shows that these compounds are formed in the proportion required by the second equation.

In the experiments an unknown quantity of pure nitrogen iodide was suspended in water and treated with an excess of decinormal sulphuric acid. After standing for about fifteen minutes to complete the decomposition, light being entirely excluded, decinormal sodium sulphite was added until the last trace of free iodine disappeared.

The total hypoiodous acid produced in the hydrolysis is measured by half the sulphite titre, since the sulphite measures the iodine liberated, and this is the same whether liberated previously to or during the actual titration by either the hypoiodous acid or the iodic acid yielded by it. The solution was next neutralized by caustic potash, and the total iodide estimated by silver nitrate, and finally excess of potash was added and the ammonia distilled off into standard acid.

From the sulphite titre, the amount of ammonia that should be liberated in the hydrolysis, assuming it to take place according to the above reaction, can be calculated and compared with the amount actually obtained. The agreement in every case was found to be within the limits of experimental error. From the sulphite titre also the amount of iodine contained in the portion of the nitrogen iodide hydrolyzed is obtained, while the iodine contained in the whole of the nitrogen iodide is given by the silver titre. The percentages undergoing hydrolysis and decomposition into nitrogen and hydriodic acid, respectively, can therefore be calculated:

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[1] The evidence for the formation of hypoiodous acid in this and similar reactions is largely indirect. If the acid product, however, be distilled immediately after the escape of the iodine, a very small quantity of a volatile compound, capable of liberating iodine from potassium iodide, passes over. This is probably a trace of hypoiodous acid which has not passed over with the iodine and has escaped transformation.

$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ = free iodine + iodine liberated by iodic acid during titration.	$\frac{N}{10}$ $AgNO_3$ = $\frac{N}{10}$ I present in whole of nitrogen iodide used = *a*.	$\frac{1}{2}\left(\frac{N}{10}\ \frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ HOI formed by hydrolysis of a portion of the nitrogen iodide = *b*.	Amount of $\frac{N}{10}$ NH_3 that should be produced in hydrolysis calculated from amount of hypoiodous acid produced.	$\frac{N}{10}$ NH_3 actually obtained in distillation.	$a-b = \frac{N}{10}$ HI obtained by decomposition of a portion of the nitrogen iodide into nitrogen and hydriodic acid.	Percentage of nitrogen iodide used which decomposed into nitrogen and hydriodic acid.
cc.	cc.	cc.	cc.	cc.	cc.	
56.7	32.8	28.35	18.9	18.9	4.45	13.5
41.8	23.9	20.9	13.9	13.9	3.0	12.5
27.2	16.2	13.6	9.06	9.1	2.6	16.0

These experiments and the fact that iodic acid is always produced prove that the greater part of the nitrogen iodide hydrolyzes under the influence of the acid.

To complete the proof it is necessary to show that the amount of nitrogen evolved corresponds with the remainder. The apparatus shown in the figure was employed:

It consisted of a bottle of about 100 cc. capacity, inside which a small tube was sealed. The bottle was ground on to a long glass tube of very narrow bore, which was attached to a measuring burette. In the experiments a convenient quantity of moist crystalline nitrogen iodide was placed in the inner, and about 40 cc. of decinormal sulphuric acid in the outer, compartment. The apparatus was then connected with the measuring burette and allowed to stand for twenty minutes in a deep cellar without windows, where the temperature did not vary 0°.1 in twenty-four hours. The acid was then run on to the nitrogen iodide. After two hours, when all action had entirely ceased, the evolved gas was measured,[1] and the other products of the decomposition estimated. The liquid was first titrated with sodium sulphite, then the ammonia was dis-

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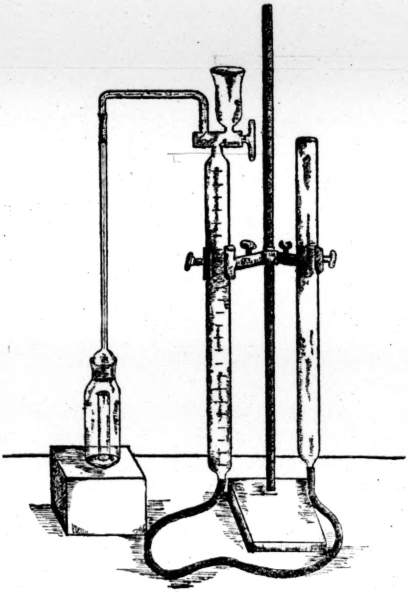
[1] The gas was shown to be pure nitrogen in a separate experiment.



tilled off after rendering alkaline with potash, and finally the total iodine present was determined by distillation with sulphuric acid and iron alum :

$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right) = a$. cc.	$\frac{a}{2} = \frac{N}{10}$ HOI produced. cc.	$\frac{N}{10}$ I obtained from nitrogen iodide, from which amount of latter used can be calculated. cc.	$\frac{N}{10}$ NH_3 produced in reaction. cc.	Nitrogen evolved in cubic centimeters at 0° and 760 mm. cc.	Nitrogen that should have been evolved calculated from amount of nitrogen iodide used and amount of hypoiodite formed. cc.	Nitrogen that should have been evolved calculated from amount of nitrogen iodide used and amount of ammonia produced. cc.
35.7	17.85	20.7	12.0	2.11	2.12	2.01
35.4	17.7	21.4	11.6	2.91	2.76	2.98

The close agreement between the amounts of nitrogen actually measured and those calculated, both from the amount of hypoiodite and from the amount of ammonia produced, show that the hypothesis of two reactions taking place simultaneously is completely justified.

Action of Phosphoric, Boric, and Acetic Acids upon Nitrogen Iodide.

These three acids act upon nitrogen iodide much as dilute sulphuric acid does. Two reactions go on simultaneously; a certain proportion, varying with the acid, breaks up into hydriodic acid and nitrogen, while the remainder is hydrolyzed, yielding an ammonium salt and hypoiodous acid, or the products of its transformation. The experiments were carried out much as with sulphuric acid.

With boric acid decomposition was much slower and the percentage hydrolyzed much smaller than with the stronger acids; the same, to a less degree, is true of acetic acid.

During the decomposition of nitrogen iodide by boric acid, small quantities frequently explode spontaneously under the surface of the liquid. As a rule, these explosions are not sufficiently violent to break the flask or splash the contents, and analyses of the products after such explosions show that in them the compound simply breaks down suddenly into nitrogen and hydriodic acid. The ammonia and hypoiodous acid are found to be produced in the same relative quantities as when no explosion occurs, the only difference being that a smaller percentage is hydrolyzed.

Decinormal solutions of phosphoric and acetic acids were used, while, as a decinormal solution of boric acid $\frac{H_3BO_3}{3 \times 10}$ decomposes nitrogen iodide rather slowly, a stronger solution containing 5 grams to the liter was used.

In the experiments recorded in the following table, numbers 1 and 2 were made with phosphoric acid, 3 and 4 with boric, and 5 and 6 with acetic acid :

Number of experiment.	$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ = free iodine + iodine liberated by iodic acid during titration. cc.	$\frac{N}{10}$ $AgNO_3$ = $\frac{N}{10}$ I present in whole of nitrogen iodide used = *a*. cc.	$\frac{1}{2}\left(\frac{N}{10}\ \frac{Na_2SO_3}{2}\right)$ = $\frac{N}{10}$ HOI formed by hydrolysis of portion of the nitrogen iodide = *b*. cc.	Amount of $\frac{N}{10}$ NH_3 that should be produced in hydrolysis calculated from amount of hypoiodous acid produced. cc.	$\frac{N}{10}$ NH_3 actually obtained in distillation. cc.	$a-b$ = $\frac{N}{10}$ HI obtained by decomposition of a portion of the nitrogen iodide into nitrogen and hydriodic acid. cc.	Percentage of nitrogen iodide used which decomposed into nitrogen and hydriodic acid.
1	42.1	24.4	21.05	14.03	13.9	3.35	13.7
2	40.6	23.6	20.3	13.53	13.5	3.3	13.9
3	44.1	36.4	22.05	14.7	14.6	14.35	39.4
4	36.2	30.4	18.1	12.06	12.0	12.3	40.4
5	36.7	23.3	18.35	12.23	12.2	4.95	21.2
6	40.6	26.3	20.3	13.53	13.6	6.0	22.8

A solution of oxalic acid also decomposes nitrogen iodide just as acetic acid does, the two usual reactions taking place simultaneously, but, as hypoiodous acid readily oxidizes oxalic acid, carbon dioxide is also produced.

Action of Hydrochloric Acid upon Nitrogen Iodide.

The addition of strong hydrochloric acid to dry nitrogen iodide causes an immediate explosion. The action of dilute hydrochloric acid upon the moist substance is less violent and can be investigated. A normal solution of hydrochloric acid, when added in excess to nitrogen iodide suspended in water, rapidly decomposes it, bubbles of nitrogen are given off, and a red-brown solution containing much iodine monochloride and a small quantity of free iodine results. If this solution be repeatedly extracted with ether, the colorless residual liquid is found to contain ammonium chloride, free hydrochloric acid, and a very small quantity of iodic acid.

The fact that iodic acid is found leads to the conclusion that the first action of hydrochloric, like that of other acids, is to induce hydrolysis. Most of the hypoiodous acid thus produced then interacts with hydrochloric acid, forming water and iodine monochloride, but a portion escapes this action and becomes transformed into iodine and iodic acid. This is possible, since the hydrochloric acid is added to the nitrogen iodide, and therefore, at first, is not present in excess, and since iodic acid, when formed, is not at the ordinary temperature able to react with hydrochloric acid. At the same time, as in other cases, a portion of the nitrogen iodide breaks down into nitrogen and hydriodic acid, the latter of which reacts either with the hypoiodous acid or the iodine monochloride to form a further and much larger quantity of free iodine. The iodine, iodine monochloride, and iodic acid are together equivalent to the hypoiodous acid produced, and on estimating these by sulphite, and the ammonia formed by distillation with potash, it is found that the ammonia calculated from the sulphite titre corresponds with that actually obtained, proving that all are formed from nitrogen iodide by hydrolysis.

In presence of the excess of hydrochloric acid, it is not easy, after titration with sulphite, to estimate directly the total hydriodic acid, but this can be obtained, and consequently the total amount of nitrogen iodide used, by titrating with silver nitrate and subtracting from the titre the amount of hydrochloric acid originally added. The percentage decomposing into nitrogen and hydriodic acid can thus be calculated.

$\frac{N}{10}\left(\frac{Na_2SO_3}{2}\right)$ = free iodine + iodine liberated by ICl and HIO_3 during titration. cc.	$\frac{N}{10}$ I contained in nitrogen iodide used = *a*. cc.	$\frac{1}{2}\left(\frac{N}{10}\ \frac{Na_2SO_3}{2}\right) = \frac{N}{10}$ HOI formed by hydrolysis of a portion of the nitrogen iodide = *b*. cc.	Amount of $\frac{N}{10}$ NH_3 that should be produced in hydrolysis calculated from amount of HOI produced. cc.	$\frac{N}{10}$ NH_3 actually obtained in distillation. cc.	$a-b = \frac{N}{10}$ HI obtained by decomposition of a portion of the nitrogen iodide into nitrogen and hydriodic acid. cc.	Percentage of nitrogen iodide used which decomposed into nitrogen and hydriodic acid.
68.4	37.8	34.2	22.8	22.7	3.6	9.52
66.2	38.2	33.1	22.06	22.1	5.1	13.37

If, instead of adding hydrochloric acid to the moist compound, pure amorphous nitrogen iodide suspended in water be very gradually added to a large excess of decinormal hydrochloric acid, the whole is hydrolyzed, no bubbles of nitrogen are evolved, and no iodine is set free, but a clear orangecolored solution results, containing, besides excess of hydrochloric acid, only iodine monochloride and ammonium chloride. The iodine monochloride can be completely extracted by repeatedly shaking the product with ether and, after such extraction, the resulting liquid is colorless, and contains no trace of iodic acid.

The following experiments show that the iodine monochloride then corresponds with the ammonia formed :

$\frac{N}{10}$ NH_3 obtained by distillation with KOH.	Amount of $\frac{N}{10}$ ICl that should be produced from HOI formed by hydrolysis of nitrogen iodide yielding the quantity of ammonia obtained.	Amount of $\frac{N}{10}$ ICl actually estimated by sodium sulphite.
cc.	cc.	cc.
18.5	27.75	27.85
21.3	31.95	31.9

In conclusion, it may be mentioned that the results obtained with hydriodic and hydrocyanic acids and those with hydrochloric acid, where iodine monochloride only is formed, can equally well be represented as direct interaction between nitrogen iodide and the acid by equations, such as

$$N_2H_3I_3 + 5HI = 3I_2 + 2NH_4I ;$$

and

$$N_2H_3I_3 + 3HNC = 2NH_3 + 3INC.$$

The fact, however, that iodic acid is produced when strong hydrochloric is added to nitrogen iodide, and that with all acids incapable of reacting with hypoiodous acid, hydrolysis undoubtedly occurs, renders it more probable that here too the same happens, and that the iodine, cyanogen iodide, and iodine monochloride are subsequently formed. In any case, by the aid of such an hypothesis, the reaction can be conveniently grouped and followed.

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THE FORMATION AND CONSTITUTION OF NITROGEN IODIDE.

By F. D. Chattaway and K. J. P. Orton.

In the preceding papers it has been shown that nitrogen iodide is a perfectly definite chemical compound, obtainable in a crystalline form. All the methods of preparation yet known yield only a single substance, the composition of which is represented by the formula $N_2H_3I_3$. With this knowledge of its composition we have been able to follow quantitatively its reactions.

Its oxidizing action may be represented by the equation

$$N_2H_3I_3 + 3H_2O + (R) = 2NH_4I + HI + R(O_3),$$

where R stands for any reducing agent. The iodine present in nitrogen iodide therefore exerts twice its normal oxidizing action.

Under all circumstances nitrogen iodide shows a tendency to break down into nitrogen and hydriodic acid, thus :

$$N_2H_3I_3 = N_2 + 3HI.$$

This decomposition takes place with great rapidity under the influence of light.

There is but little doubt that, in the explosion of nitrogen iodide, a similar decomposition takes place. When treated with acids nitrogen iodide frequently explodes, and we have shown that, under these circumstances, where there is no loss of the substances formed, a much greater amount of the iodide decomposes into nitrogen and hydriodic acid than occurs in the absence of explosion.

In the ready decomposition of nitrogen iodide by acids and alkalies, two separate reactions take place concomitantly, hydrolysis and a decomposition into nitrogen and hydriodic acid. Thus, with alkalies :

$$N_2H_3I_3 + 3KOH = 2NH_3 + 3KOI\,;$$
$$3KOI = KIO_3 + 2KI\,;$$

with acids :

$$N_2H_3I_3 + 3H_2O + 2H\bar{A} = 2NH_4\bar{A} + 3HOI.$$

The final products are determined by the nature of the acid. Hydrochloric and hydrocyanic acids react with the hypoiodous acid to form iodine monochloride and cyanogen iodide ; hydriodic acid to liberate iodine. With other acids the final products are the ammonium salt of the acid, iodic acid, and iodine.

These reactions leave no doubt that in nitrogen iodide neither iodine nor hydriodic acid is present in loose molecular combination, such as occurs in periodides or acid iodides. Each atom of iodine is monovalent, and directly linked with nitrogen.

From a study of the action of iodine on potash, soda, and ammonia, Schönbein concluded that in all cases the initial products were iodide and a hypoiodite, and suggested that nitrogen iodide was formed by a decomposition of ammonium hypoiodite and not by direct substitution. This view was endorsed by Selewanow, who attempted to show qualitatively[1] that a hypoiodite remained in the ammoniacal solution after precipitation of nitrogen iodide.

To elucidate this point fully, we have studied quantitatively the actions of iodine and iodine monochloride on ammonia, the oxidation of arsenite being used as a means of estimating hypoiodite, the formation of which always accompanies the formation of nitrogen iodide.

In the case of free iodine exactly half, and in the case of iodine monochloride the whole of the iodine present appears as nitrogen iodide and hypoiodite, or as ammonium iodide and iodate, the transformation products of the latter. Further, we find that addition of ammonia to a solution of an alkaline hypoiodite is followed directly by the separation of nitrogen iodide.

When an alkaline solution of potassium hypoiodite of known strength is used, and the hypoiodite estimated in the filtrate from the precipitated nitrogen iodide, the iodine as hypoiodite in the filtrate is found to be less than the iodine as hypoiodite originally present, by an amount which equals the iodine as nitrogen iodide. The latter is, therefore, formed at the expense of the hypoiodite, and the following equations must represent the action of iodine and iodine monochloride on solutions of ammonia :

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[1] He used, as a test for hypoiodite, the liberation of iodine on addition of potassium iodide.

$$I_2 + 2NH_4OH = NH_4I + NH_4OI;$$
$$ICl + 2NH_4OH = NH_4Cl + NH_4OI;$$
$$3NH_4OI = N_2H_3I_3 + 2H_2O + NH_4OH.$$

The reaction represented by the last equation is never complete, a certain small amount of hypoiodite remaining in the solution and becoming transformed into iodate and iodide.

Thus, though in the action of iodine on ammonia only half the iodine originally becomes iodide, this quantity increases somewhat at the expense of the hypoiodite.

Exact experiments further show that treatment of nitrogen iodide by a solution of ammonia leads to the formation of ammonium hypoiodite.

The concentration of hypoiodite reached is always very small,[1] and attains its maximum value in the course of half an hour ; it is constant for a given concentration of ammonia and a given temperature, but increases with the increase of either.

The simplest explanation[2] of all the observed facts appears to be that ammonium hypoiodite is very unstable, and when formed immediately decomposes into nitrogen iodide and ammonia. The action, however, is a reversible one, and consequently a small amount of ammonium hypoiodite remains unaltered in the mother-liquor, while a corresponding amount is formed in a solution of ammonia placed in contact with nitrogen iodide.

If we have a reversible action represented by

$$N_2H_3I_3 + NH_4OH + 2H_2O \rightleftarrows 3NH_4OI,$$

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[1] The maximum concentration, we have observed, was such that 100 cc. of the ammoniacal solution oxidized 3.3 cc. of $\frac{N}{10}$ arsenite.

[2] It is impossible to say definitely whether the substance dissolved in the ammoniacal supernatant liquor is nitrogen iodide itself or the product of its hydrolysis, ammonium hypoiodite, as either would oxidize arsenite. From a consideration, however, of the action of other alkalies and of hot solutions of ammonia on nitrogen iodide and also of the action of ammonia on solutions of hypoiodites, it is almost certain that the solution contains hypoiodite.

the equation $kx.w.c'' = (c')^3$ should apply to the state of equilibrium, where $x =$ the concentration of the solid nitrogen iodide (which is constant), $w =$ the concentration of the water (which is very large and does not appreciably vary), c'' that of the NH_4OH, c' that of the NH_4OI. Then $\frac{(c')^3}{c''} = k.x.w =$ a constant.

The following table gives the results of experiments with four concentrations of ammonia at a temperature of 12° C.

Concentration of ammonia in gram-molecules per liter $= c''$.	Concentration of hypoiodite in gram-molecules per liter $= c'$.	$('c)^3$.	$\frac{(c')^3}{c''}$.
0.1	0.00023	0.012×10^{-18}	0.12×10^{-8}
0.5	0.000385	0.060×10^{-18}	0.12×10^{-8}
1.0	0.000525	0.14×10^{-18}	0.14×10^{-8}
3.0	0.0007	0.33×10^{-18}	0.11×10^{-8}

The value of c' is, however, so extremely small that little stress can be laid on the results. They confirm, however, so far as they go the above explanation.

There is very little direct evidence from which to deduce a constitutional formula for this so-called nitrogen iodide. It may be supposed with a fair degree of certainty that the two nitrogen atoms are linked together, and that the compound is represented by one of the formulæ, $NH_3 : NI_3$ or $NH_2I : NHI_2$.

All the evidence we have goes to show that the former is the more likely. Nitrogen iodide, which has been allowed to stand under water, becomes much more liable to explode, and analyses of partly decomposed material point to a disintegration of the molecule and a liberation of very unstable NI_3 in the residue, but this latter compound cannot be isolated, and only exists, if at all, in the presence of a large excess of free iodine.

EXPERIMENTAL PART.

Action of Iodine on a Solution of Ammonia.

In these experiments we employed an approximately decinormal solution of iodine in chloroform. Solutions of iodine in potassium iodide led to inexact results, owing probably to the large excess of iodide necessarily present.[1] A known quantity of the chloroform solution was run into a known quantity of a solution of ammonia. The flask containing the mixture was shielded carefully from the light and shaken for two or three minutes. The nitrogen iodide was then filtered off through ignited asbestos by the help of a filter-pump and washed three or four times with water. The iodine in the nitrogen iodide was estimated by standard sodium sulphite. The filtrate was acidified and the iodine set free titrated. It is a measure of the hypoiodite remaining after the nitrogen iodide is precipitated, and is independent of the transformation into iodate and iodide, as is shown by the following equations:

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[1] It was stated (J. Chem. Soc., 1896) that more than half the iodine used could, under certain conditions, be converted into nitrogen iodide. This is not correct. The error was caused by the use of a solution of iodine in potassium iodide.

$$3HIO + 3HI = 3H_2O + 3I_2;\quad 3HIO = HIO_3 + 2HI;$$
$$HIO_3 + 5HI = 3H_2O + 3I_2.$$

Amount of iodine used as cubic centimeters of a decinormal solution.	Amount of 3.3 N solution of ammonia used. cc.	Amount of iodine in nitrogen iodide expressed as cubic centimeters of a decinormal solution.	Amount of iodine in ammonium hypoiodite expressed as cubic centimeters of a decinormal solution.	Total amount of iodine in nitrogen iodide and in ammonium hypoiodite expressed as cubic centimeters of a decinormal solution.	Half amount of iodine used.
51.6	20	24.6	1.1	25.7	25.8
48.4	20	23.6	0.6	24.2	24.2
41.2	40	19.8	0.8	20.6	20.6

The agreement between columns 5 and 6 is very good. In the interaction of iodine and ammonium hydroxide, therefore, one-half the iodine becomes initially ammonium iodide and half ammonium hypoiodite and nitrogen iodide.

Action of Iodine Monochloride on Ammonia.

A known quantity of a half-normal solution of iodine monochloride was run into a known quantity of a 3.3 N-solution of ammonia. The solution was screened from light and shaken for two or three minutes. The nitrogen iodide was then filtered off and the iodine estimated in it and in the filtrate as previously described.

Iodine contained in iodine monochloride used expressed as cubic centimeters of a decinormal solution.	Amount of 3.3 N-ammonia solution used. cc.	Amount of iodine in nitrogen iodide produced expressed as cubic centimeters of a decinormal solution.	Amount of iodine in ammonium hypoiodite produced expressed as cubic centimeters of a decinormal solution.	Total amount of iodine in nitrogen iodide and in ammonium hypoiodite expressed as cubic centimeters of a decinormal solution.
23.6	20	22.5	1.1	23.6

A large number of experiments gave exactly similar results. The agreement of columns 1 and 5 shows that the whole of the iodine becomes nitrogen iodide and ammonium hypoiodite.

Action of Ammonia on a Solution of Potassium Hypoiodite.

The addition of ammonia to alkaline solutions of potassium hypoiodite, leads under suitable conditions to an immediate separation of nitrogen iodide. When the concentration of the hypoiodite is within certain limits (below 0.03 and above 0.007 gram-molecule per liter) the nitrogen iodide is deposited in the crystalline form.

In these experiments we estimated the amount of hypoiodite in the original solution before the addition of ammonia, and in the alkaline filtrate after the nitrogen iodide had been removed. A standard solution of sodium arsenite was employed to estimate the hypoiodite. This oxidation of arsenite by hypoiodite was noted by Lonnes and used by him in the estimation of the latter.

A liter of the alkaline hypoiodite solution was made up by adding a solution of iodine monochloride in hydrochloric acid to a solution of potash, the latter being in large excess. The alkalinity of the mixture was that of a 3 N/10 solution. At intervals two quantities, each of 100 cc., were simultaneously withdrawn. One was immediately titrated by standard arsenite and to the other 10 cc. of 0.880 ammonia solution were added. After standing for two minutes in the dark, the nitrogen iodide was filtered off and washed with water two or three times. The hypoiodite in the filtrate and the iodine in the nitrogen iodide formed were then quickly estimated in the same manner.[1]

Concentration of KOH in gram-molecules per liter.	Iodine present in 100 cc. as hypoiodite before addition of ammonia in cc. of $\frac{N}{10}$ solution.	Iodine present in nitrogen iodide obtained from 100 cc. of KOI solution in cc. of $\frac{N}{10}$ solution $= a$.	Iodine present as hypoiodite in filtrate from the nitrogen iodide in cc. of $\frac{N}{10}$ solution $= b$.	$(a+b)$ = iodine present as hypoiodite + iodine in nitrogen iodide in cc. of $\frac{N}{10}$ solution.
0.3	16.8	10.1	6.4	16.5
0.3	8.05	0.85	6.9	7.75

The numbers in column 2 should equal those in column 5. The latter are always a little too low. This would be expected from the loss of hypoiodite unavoidably incurred through conversion into iodate and iodide in the time occupied in filtering off the nitrogen iodide and titrating the filtrate. It is very clear, however, that the nitrogen iodide is formed at the expense of the hypoiodite. The precipitation of the former is accompanied by a proportional decrease of the latter in the solution.

Many experiments have been made with exactly similar results. The influence of alteration in the relative proportions of the potassium and ammonium hydroxides show that, as the concentration of the ammonia increases until the ammonia and potash are in equivalent proportions, the yield of nitrogen iodide rapidly increases. With further increase of the quantity of ammonia the yield of nitrogen iodide slowly reaches a maximum and then falls off. A large excess of potash exercises only a slight influence on the yield, provided the ammonia is present in equivalent excess. In the preparation of the solution of hypoiodite, it has been found that if the admixture of the solutions of iodine monochloride and potassium hydroxide is made with sufficient care and rapidity, no iodine is set free, and the whole of the iodine is for a short time present as hypoiodite. In the experiments, the results of which are given in the following table, the solution of ammonia was added to the hypoiodite solution within fifteen seconds of its preparation. After standing for two minutes the nitrogen iodide was filtered off and estimated.

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[1] It has been found that solutions of ammonium hypoiodite are converted very slowly into iodate and iodide, some weeks being required for the complete disappearance of the hypoiodite. They offer a marked contrast to solutions of potassium hypoiodite, which completely decompose in twenty-four hours.

Concentration of KOH in gram-molecules per liter.	Iodine as hypoiodite present at moment of adding ammonia in cc. of $\frac{N}{10}$ solution.	Concentration of hypoiodite in gram-molecules per liter.	Concentration of ammonia in gram-molecules per liter.	Iodine in nitrogen iodide obtained in cc. of $\frac{N}{10}$ solution.	Percentage of iodine used which was converted into nitrogen iodide.
0.40	35.8	0.0358	0.0585	15.4	43.0
0.40	35.8	0.0358	0.117	18.1	50.5
0.40	35.8	0.0358	0.234	22.7	63.3
0.40	28.6	0.0358	0.488	19.2	67.2
0.46	24.0	0.024	0.936	18.2	76.0
0.46	24.0	0.024	1.87	18.1	75.0
0.46	24.0	0.024	6.0	17.4	72.0

In the following table are given the results of several experiments which demonstrate clearly the fact that nitrogen iodide only separates from solutions of alkaline hypoiodites when the concentration of the latter is above a certain value.

Concentration of KOH in gram-molecules per liter.	Iodine as hypoiodite present at moment of adding ammonia in cc. of $\frac{N}{10}$ solution = *a*.	Concentration of hypoiodite before addition in gram-molecules per liter.	Concentration of ammonia in gram-molecules per liter.	Iodine in nitrogen iodide obtained in cc. of $\frac{N}{10}$ solution = *b*.	Iodine as hypoiodite after precipitation of nitrogen iodide as cc. of $\frac{N}{10}$ solution = (*a*—*b*).	Concentration of hypoiodite after precipitation of nitrogen iodide in gram-molecules per liter.
0.3	3.86	0.0038	1.6	0.0	3.8	0.0038
0.54	7.7	0.005	6.0	0.0	7.7	0.005
0.3	8.06	0.0073	1.6	0.85	7.2	0.0065
0.57	16.2	0.015	1.6	8.0	8.2	0.0076

The formation of the nitrogen iodide ceases when the concentration of ammonium hypoiodite in the solution falls to the limit at which it is capable of existing under the conditions. A final state of equilibrium is then established between the potassium and the ammonium hypoiodites, which is only gradually altered by the slow transformation into iodate and iodide.

Action of Ammonium Hydroxide on Nitrogen Iodide.

The action of a hot solution of ammonia on nitrogen iodide resembles that of the alkaline hydroxides, the major portion is hydrolyzed, forming finally iodate and iodide, while a smaller part decomposes into nitrogen and hydriodic acid. As ammonium hypoiodite is the first product of the hydrolysis, and as this can, when the concentration is sufficient, transform into nitrogen iodide, on rapidly cooling such a hot solution in which the nitrogen iodide has only just disappeared, crystals of the latter again separate. If the solution be cooled slowly or the boiling continued for a short time, no crystals are deposited, as the hypoiodite at the high temperature is rapidly and completely transformed into iodide and iodate. The following experiments, carried out with a hot solution of ammonia exactly as described under the action of hot potash, show the variable proportion in which the two actions take place:

$\frac{N}{10}\ \frac{Na_2SO_3}{2}$.	Total iodine in nitrogen iodide used as cc. of an $\frac{N}{10}$ solution.	Ratio of iodine as iodate to total iodine.	Percentage of nitrogen iodide decomposed into nitrogen and hydriodic acid.
28.2	16.4	0.859 : 3	14.02
20.6	12.4	0.830 : 3	16.93
31.3	20.1	0.778 : 3	22.13

When nitrogen iodide is suspended in a cold solution of ammonia similar actions take place but very gradually, bubbles of nitrogen are but slowly evolved, and a large quantity of nitrogen iodide remains with little apparent change for months, although an exceedingly slow conversion of nitrogen iodide into ammonium iodide and iodate is continually progressing.

Ammonium hypoiodite, however, appears directly in the solution, and in a short time has attained its maximum concentration, which is always very small. The concentration of the hypoiodite increases with rise of temperature and with increased concentration of the ammonium hydroxide. For a given concentration of ammonia and a given temperature, the ultimate concentration of hypoiodite is the same, whether the starting-point is iodine monochloride and ammonia or nitrogen iodide and ammonia.

In the experiments made about 0.5–1 gram of pure crystallized nitrogen iodide was placed in a stoppered bottle containing 300 cc. of a solution of ammonia of known strength. A number of these were allowed to stand in a dark cellar where the temperature did not vary more than 0°.5 for days. At intervals 100 cc. of the supernatant liquid were withdrawn and filtered through ignited asbestos. To estimate the hypoiodite, excess of standard arsenite was added and carbon dioxide was passed in until the smell of ammonia became faint. By means of standard iodine solution, the excess of arsenite was then estimated. Blank experiments, made with solutions of ammonia of the strength used, show that neither the various operations nor the presence of the large quantity of ammonium bicarbonate in any way affected the accuracy of the titration of arsenite by iodine.

	Series I: Nitrogen iodide in contact with solution of NH_4OH for twenty-four hours. Temp. = 12° C.		Series II: Nitrogen iodide in contact with solution of NH_4OH for three days. Temp. = 12° C.	
Concentration of NH_3 in gram-molecules per liter.	Amount of $\frac{N}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.	Amount of $\frac{N}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.
0.12	0.48	0.00024	0.51	0.00025
0.24	0.55	0.00027	0.56	0.00028
0.48	0.68	0.00034	0.72	0.00036
1.08	1.05	0.00052	0.92	0.00046
2.16	1.50	0.00075	1.53	0.00076
3.0	1.70	0.00085	1.67	0.00083

A comparison of these two series shows the accuracy attainable and the influence of the concentration of ammonia.

	Series III : Nitrogen iodide in contact with a solution of NH_4OH for twenty-four hours. Temp. = 12° C.		Series IV : Nitrogen iodide in contact with a solution of NH_4OH for one and a half hours. Temp. = 29° C.	
Concentration of NH_3 in gram-molecules per liter.	Amount of $\frac{N}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.	Amount of $\frac{N}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.
0.1	0.46	0.00023	0.94	0.00047
0.5	0.79	0.00038	1.79	0.00090
1.0	1.05	0.00052	2.24	0.00112
3.0	1.40	0.00070	3.33	0.00167

Series III. and IV. demonstrate the influence of temperature. A rise in temperature of 17° C. (from 12° C. to 29° C.) doubles the concentration of the hypoiodite. As a consequence, on rapidly cooling a few cubic centimeters of the most concentrated ammoniacal solution of hypoiodite, crystals of nitrogen iodide separate.

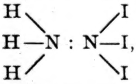
In the following experiments a solution of iodine monochloride was added to a solution of ammonia, the further procedure being as described above for Series III :

Concentration of NH_3 in gram-molecules per liter.	Amount of $\frac{N}{10}$ arsenite oxidized. cc.	Concentration of hypoiodite in gram-molecules per liter.
0.088	0.37	0.00019
0.5	0.74	0.00037
1.0	0.97	0.00049
3.0	1.4	0.00070

A comparison of results shows that the same final state of equilibrium is attained whether the starting-point is nitrogen iodide and ammonia or iodine monochloride and ammonia.

Study of Various Stages in the Decomposition of Nitrogen Iodide by Water and Dilute Sulphuric Acid.

The actions which take place when nitrogen iodide is completely decomposed by water or dilute acids have already been described. A careful study has been made of the course of these reactions, as it appeared likely to throw light upon the structure of the nitrogen iodide molecule.

Assuming, for example, the compound to have the formula  it seemed possible that the molecule might in the first instance break down into NI_3 and NH_3 when hydrolyzed by water or dilute acids. The NH_3 might then be washed away either alone or combined with acid, leaving the NI_3 as an insoluble residue mixed with still undecomposed nitrogen iodide.

An estimation of the ratio of N to I in the partially decomposed product would then give some information as to the molecular structure.

The problem is complicated by the fact that, in such a partial decomposition, iodine is produced from the first and remains in the insoluble residue. This free iodine can, however, be estimated and the ratio of nitrogen to combined iodine determined in any mixture of compounds, since such combined iodine must be directly attached to the nitrogen in all.[1]

The decomposition of a large quantity of pure nitrogen iodide by water has, therefore, been quantitatively studied. About 0.5 kilogram of the pure amorphous compound was decomposed by water in absence of light. At first it was placed in a large funnel, closed by a plug of asbestos, and water allowed to percolate through the mass. Afterwards, as such partially decomposed nitrogen iodide is extremely sensitive and the local explosions caused by the escape of bubbles of gas become dangerous, it was transferred to a stout porcelain vessel and water allowed to run slowly over it.

At short intervals, at first every few minutes, then every hour, and finally every day, portions were removed, carefully washed and analyzed. Some 80 analyses altogether were made of which a few, typical of different stages of decomposition, are given in the following table in the relative order in which they were made. Similar results are obtained when nitrogen iodide is decomposed by dilute sulphuric acid, although the action is much more rapid :

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[1] See "The Composition of Nitrogen Iodide," This JOURNAL, **24**, 144.

Number of analysis.	$\frac{N}{10}$ $\frac{Na_2SO_3}{2} = a$. cc.	$\frac{N}{10}$ NH_3 required to neutralize solution $= \frac{N}{10}$ HI produced in free state. cc.	$\frac{N}{10}$ $AgNO_3$ required $= \frac{N}{10}$ HI formed $= b$. cc.	$\frac{N}{10}$ NH_3 formed. cc.	$x = \frac{N}{10}$ I present as nitrogen iodide. cc.	$y = \frac{N}{10}$ I present as free element. cc.	Percentage of total iodine present as free element.	Ratio between NaI in the mixed substances containing I attached to N in the partially decomposed product.
1	93.6	15.6	46.8	31.2	46.8	0.0	0.0	2 : 3
2	36.7	6.7	18.5	11.8	18.2	0.3	1.62	1.94 : 3
3	55.9	10.8	28.2	17.4	27.7	0.5	1.77	1.88 : 3
4	62.3	15.7	31.6	15.9	30.7	0.9	2.85	1.55 : 3
5	86.8	26.6	45.3	18.7	41.5	3.8	8.39	1.35 : 3
6	65.7	28.1	39.4	11.3	26.3	13.1	33.25	1.28 : 3
7	66.6	33.5	42.9	9.4	23.7	19.2	44.78	1.18 : 3

It is seen that the ratio of nitrogen to iodine atoms in the residue, excluding the free element, continually decreases as the decomposition proceeds, and that it slowly approaches the ratio N : 3I required by the substance NI_3. This result makes it very probable that the constitution of the molecule really is represented by the formula given above, and that, on decomposition by water or dilute acids, those molecules which do not break down into N and HI first decompose into NI_3 and NH_3, and that the former is then hydrolyzed.

If the ratio N : 3I could be ultimately obtained, and the results were absolutely to be relied upon, the formula would be established. The large percentage of iodine present when this ratio is nearly reached introduces, however, a possibility of error and, although the constitution $NH_3 : NI_3$ is rendered very probable, it cannot be regarded as conclusively proved.

In conclusion we desire to thank Mr. R. T. Evans and Mr. W. L. Blackman, who have rendered us great assistance in various parts of the work.

The following is a complete list of previous researches on the subject:

Courtois: Ann. Chim., **88**, 304 (1813); Vauquelin: *Ibid.*, **90**, 239 (1814); Gay-Lussac: *Ibid.*, **91**, 5 (1814); Colin: *Ibid.*, **91**, 252 (1814); Davy: *Ibid.*, **92**, 89, and Trans. Roy. Soc., **86** (1814); Sérullas: Ann. chim. phys. [2], **22**, 172 (1825), and **42**, 200 (1829); Mitscherlich: Gmelin's Chemistry, Vol. 2, 465; André: Jour. Pharm., **22**, 137 (1836); Millon: Ann. chim. phys. [2], **69**, 78 (1838); Marchand: J. prakt. Chem., **19**, 1 (1840); Bineau: Ann. chim. phys. [2], **67**, 225 (1836), and [3], **15**, 71 (1845); Cass: Jour. Pharm. Chim., 52 (1851); Bunsen: Ann. Chem. (Liebig), **84**, 1 (1852); Gladstone: J. Chem. Soc., **4**, 34 (1852), and **7**, 51 (1853); Schönbein: J. prakt. Chem., **84**, 385 (1861); Stahlschmidt: Ann. phys. Chem., **29**, 421 (1863); Guthrie: J. Chem. Soc., **16**, 239 (1863); Stas: Nouvelles Recherches (Brussels), 1865, p. 157; Champion et Pellet: Bull. Soc. chim. [2], **24**, 447 (1875); Mallet: This JOURNAL, **1**, 4 (1879–1880); Guyard: Compt. rend., **97**, 526 (1883), and Ann. chim. phys. [6], **1**, 358 (1884); Raschig: Ann. Chem. (Liebig), **230**, 212 (1885); Willgerodt: J. prakt. Chem., **145**, 446 (1888); Szuhay: Ber. d. chem. Ges., **26**, 1933 (1893); Seliwanow: *Ibid.*, **27**, 1012 (1894); Chattaway: J. Chem. Soc., 1896, 1572; Losanitsch and Jovitschitsch: Ber. d. chem. Ges., **29**, 2436 (1896); Mallet: Proc. Chem. Soc., 1897, 55.

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INVESTIGATION OF THE HALPHIN COLOR TEST AS TO ITS VALUE FOR THE DETECTION OF COTTONSEED OIL.

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In 1898 there appeared in several of the chemical journals a few brief articles relating to a certain color test for the identification of cottonseed oil, as devised by Mr. Georges Halphin. After confirming the reliability of this reaction by a number of tests at that time, the somewhat modified test was, on account of its simplicity and sensitiveness, adopted by the writer for the identification of cottonseed oil in oils and fats, in preference to the Becchi and Milleau tests.

Being called upon later, in a commercial way, to defend certain claims as based upon this test, it became apparent that the real value of this reaction was not generally accepted and consequently it has been more thoroughly investigated by the writer to further test its reliability and to secure its more general recognition among chemists.

The few references to the test found in the journals give only its general principles and a few of the results obtained by the respective authors. Halphin first called attention to his reaction in 1894[1] by stating that, from the evaporated distillate from a mixture of fatty acids of a fat or oil, carbon disulphide, and zinc oxide, an amber-yellow residue is obtained with hog, beef, mutton, and goat fats, while, when cottonseed oil is present, an orange-red zinc salt is obtained. He asserted later[2] that this coloration is due to the action of the carbon disulphide rather than the zinc oxide, and further recommended the addition of free sulphur, the whole being dissolved in amyl alcohol, giving as his method of procedure the following: Mix equal parts of oil or fat, amyl alcohol, and carbon disulphide containing 1 per cent free sulphur, and heat in a saturated solution of salt for ten to fifteen minutes. If no color appears, reheat and add more of the carbon disulphide solution.

P. Soltsien[3] states that he has tried Halphin's test, and says that amyl alcohol and the salt-bath are unnecessary. He compares the color to a solution of potassium dichromate, and says that old and rancid fats do not produce the reaction, and that in colorless and clear fats 1 per cent of cottonseed oil can be recognized, while with colored fats from 2 to 5 per cent, according to the depth of color of the original sample. He states that an oil (cottonseed) heated to 200° gives the reaction unchanged, and he gives the following as not showing the coloration: Lard, strongly rancid lard, old rancid lard oil, the same mixed with tallow, sesame oil, various cheese fats, olive oil, rapeseed oil, poppy oil, camelina (German sesame) oil, cod-liver oil, arachide oil, and hazelnut oil.

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[1] Centrbl., 1894, II., 716.

[2] *Ibid.*, 1897, II., 1161.

[3] *Ibid.*, I, 1049 (1899).

D. Holde and R. Pelgry[1] confirm the Halphin reaction, but claim to have got it with thran or blubber oil, quoting Halphin as having obtained a coloration with a pure thran oil, although Halphin says this will not be confounded with the cotton oil coloration, if it is allowed to flow in a thin layer on a stirring rod. They claim that an oil heated to 250° does not give the reaction.

P. Soltsien[2] replies that an oil heated to 250° is no longer fit for use as an edible, but up to 200° the reaction is permanent. He says that the test should be heated from forty-five minutes to one hour to get the full coloration. Holde and Pelgry[3] state that the point of destruction is below 250°, somewhere between 210° and 250°.

L. Archbutt[4] has used the test on maize oil with negative results.

Other references are to be found as noted below.[5]

The writer's work corroborates to a great extent that of the above chemists, but he finds that for the proper coloration the combined action of the carbon disulphide, sulphur, and amyl alcohol is required, and that not one of these can properly be dispensed with as claimed by some. Ordinary ethyl alcohol gives the reaction with less depth of coloration than amyl alcohol, and the salt-bath is most desirable on account of the high constant boiling-point it affords.

We find, as Soltsien did, that old and rancid fats do not produce the reaction, and, further, that an old and rancid cottonseed oil or fat mixture containing it produces a weaker and more brownish reaction, even to the total obliteration of the reaction in very old fats or oils. The Becchi and Milleau tests, on the contrary, are more or less produced by such conditions. Consequently, with the Halphin test, as with other tests, the fresher the material tested the more satisfactory the results.

[1] Centrbl., I., 1085 (1899).

[2] *Ibid.*, I., 1297 (1899).

[3] *Ibid.*

[4] J. Soc. Chem. Ind., April, 1899.

[5] Chem. Rev. Fett. u. Harz-Ind., **6**, 67, and **6**, 94; Ztschr. öffent. Ch., **5**, 106; Revue de chim. Ind., Feb., 1898; Jour. Pharm. Chem. [5], 30–241, and [6], **6**, 390; The Analyst, May, '98, 114 and 131; Am. Chem. Analyst, **3**, [1] 9–11.

Soltsien has found the test sensitive to 1 per cent of cottonseed oil, while we have been able to obtain a coloration with quite a small fraction of 1 per cent under favorable conditions, *i. e.*, fresh material not too deeply colored.

As to the degree of heat applied to the original oil necessary to destroy the reaction with it, we find it to be influenced by the length of time heated, and the quality of material in contact with the oil. With glass vessels this point of neutralization lies between 315° and 320° C.,[1] slightly lower in a vacuum, while, if the vessel is of metal or contains pieces of metal, this limit is lowered more or less in proportion to the metal in contact with the oil. As an example, an oil heated half an hour in a porcelain-lined kettle at about 200° showed that the reaction was little, if any, affected; while an oil heated in a steel frying pan at 140°–150° for an hour gave no indication (or coloration) of cottonseed oil. While the metals tend to lower the point of neutralization, they do not bleach a color once produced.

The active ingredient of cottonseed oil is not merely driven off from the oil by high heat, but is completely destroyed, since the fumes arising from it, as well as the oil, give no coloration.

As to the degree of heat that would be detrimental to an oil for culinary purposes, we certainly agree with Soltsien that 250° is even excessive. The temperature of an oil for frying should not exceed 150°–160° (lards and solid fats somewhat lower), at which point it will "brown bread crumbs;" while for frying crullers the temperature will probably rise to 200°–210°.

The method of procedure, as adopted by the writer, is as follows:

Apparatus Required.—10 cc. pipettes (3); test-tubes ($1\frac{1}{8}'' \times 8''$ to 10″); saturated salt-water bath.

Reagents.—Amyl alcohol (C. P.); carbon disulphide (C. P.), containing 1 to 2 per cent fresh flowers of sulphur.[2]

Manipulation.—10 cc. each of the solutions is measured into a test-tube with 10 cc. of the oil or melted fat sample.[1] The mixture is agitated frequently and heated first in a steam-bath until the violent boiling ceases, and then placed in the boiling salt-water bath (temp. 105°–110°) for from forty-five minutes to one hour—two to three hours if only traces of oil are present—occasionally removed and agitated. The steam-bath should be used at first to prevent the first heavy fumes of carbon disulphide from igniting by contact with the open flame.

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[1] Somewhat lower temperature with longer time of heating.

[2] A higher percentage of sulphur does not improve the reaction.

Indications.—A beautiful crimson wine coloration, varying in depth according to the percentage of cottonseed oil present. If no coloration appears after two to three hours' boiling, the sample contains no cottonseed oil, while as little as 1 per cent will give indications in fifteen to twenty minutes.

If heated over four to five hours, a misleading brownish-red color is produced, even with pure lard, a result which is due to burning.

Necessarily, the first thing to be determined was whether the test is characteristic of cottonseed oil, and that alone among the various fats and oils; second, whether any compound, organic or inorganic, probably present in commercial fats and oils, such as fillers and colorings, will produce this reaction; and, third, the sensitiveness of the reaction with cottonseed oil in other fats.

Of the various fats and oils examined by the writer with this test, samples of four other oils than cottonseed oil have given colorations somewhat resembling that of the cottonseed oil reaction. These colorations were of a brownish or yellowish shade and were barely noticeable with a 5 per cent mixture in (C. P.)[2] lard, showing that, as far as these samples go, it is not a very delicate test for the oils mentioned. These four samples of sunflower, rape or colza, nigre, and poppyseed oils of foreign manufacture, as purchased in the open market and, consequently, of uncertified purity, gave, as noted, more or less of a coloration; but, when these same oils were extracted with rectified gasoline directly from their unadulterated seeds (with the exception of rape oil, which seed could not be obtained), thereby insuring absolute freedom from contamination with other oils, no coloration whatever was noticed after several hours.[1]

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[1] Five cc. each is used in routine daily tests, any indication being verified by taking 10 cc.

[2] By C. P. lard is meant lard free from any cotton oil.

It would appear from this that the samples showing colorations were not of the purest quality and contained traces of cottonseed oil, which assumption is further strengthened by observations on other samples of rape and poppy oil, which gave no reaction, and also by Soltsien's[2] negative results with them. As the method of alternating pressings of various kinds of oil seeds as practiced in most European mills, would permit of such unobserved sophistication, it seems more than probable that cottonseed oil would become more or less mixed with the various other oils in the process of manufacture, and thus give one the apparently misleading indication with the other oils. It has been found to the manufacturer's sorrow, if the Halphin test is used, next to an impossibility to handle cottonseed oil and other oils and fats through the same presses, pumps, pipes, tanks, etc., and to keep the various oils and fats free from traces of the cottonseed oil, however much care is used in rinsing out the apparatus.

I. It seems then fairly evident that the Halphin reaction is produced by none of the common edible oils and fats other than that from the cottonseed.[3]

II. Using the test mostly in connection with (hog) lards, we have used that fat as a medium for adulterants, mixing with such lards as give no trace of a reaction, various fillers and colorings; as yet we have found nothing tending to give the reaction,[4] thus establishing it as still more reliable as a characteristic test of cottonseed oil.

III. As to the sensitiveness of the reaction or the percentage of cottonseed oil shown by this test we have found it decidedly positive in lards with 1 per cent, and without doubt reliable with $\frac{1}{2}$ and even $\frac{1}{4}$ per cent; also $\frac{1}{8}$ to $\frac{1}{10}$ and even $\frac{1}{16}$ per cent of cottonseed oil in fresh colorless lards gives a noticeable faint coloration if compared with a blank test (one with a pure lard).[5]

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[1] See Table I.

[2] *Loc. cit.*

[3] See Table I.

[4] See Table II.

[5] See Table III.

Of the various grades of cottonseed oil the test works with crude, yellow, and white; and summer, winter, and (oil) stearin qualities almost equally well, being darker with the crude, and scarcely noticeably so with the yellow, than with the white, due to the original additional color; and lighter with the oil stearin, and slightly so with the summer, than with the winter, oil, indicating that the active principle of the oil is not contained in the triglycerides of stearic acid.

This test can be used more or less quantitatively by comparing, in small tubes, the depths of color produced with those of equally concentrated volumes from tests of mixtures of known percentages of oil (most satisfactorily in lards with mixtures of less than 1 per cent cotton oil).

The coloration produced by this reaction is quite stable in the dark, being only slowly affected by exposure to light and air.

A cottonseed oil or fat mixture containing a high percentage of this oil, treated with the Halphin solutions and once colored retains the color in its soap, fading after a time, and even in its fatty acids, only a small portion washing out from the fat.

This test can be applied directly to the soap or fatty acids of a fat mixture of high percentage of cotton oil if not too deeply colored, with some degree of confidence, the coloration produced being more brownish than with the neutral fat, and consequently not as delicate a reaction. The subjection of the fatty acids to an oven temperature of 100° affects the results only slightly with the higher adulterations of oil, while with the lower percentages it destroys the colorations more or less through the darkening of the acids themselves.

This reaction may be made use of to some extent in inorganic work for the recognition of free sulphur, by treating the unknown substance with a mixture of equal parts of pure cotton seed oil (bleached), amyl alcohol, and carbon disulphide free from sulphur.[1]

As to the active principle or compound in cottonseed oil that produces the Halphin reaction, technically it is not of so great importance, although scientifically it might be of considerable interest. As noted, it appears not to be contained in the stearin constituents, is influenced by the action of metals, and is destroyed by high heat, age, and decomposition. The color produced may be due to the same cause as is thought by some to produce the Becchi and Milleau reactions —volatile sulphur compounds contained in the oil; but, as Dupont and Charabut have found sulphur in olive oil, which is neutral to this test, this theory appears less probable.

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[1] See Table V.

Following are the tabulated results of a series of experiments which furnish the basis of the foregoing statements :

TABLE I.

Results with Various Oils and Fats.

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Olive oil	(A) Olive oil	France	Fresh	None other than greenish cast
“ “	(B) “ “	“	“	None other than greenish cast
“ “	“ “	New York	“	None other than greenish cast
“ “	“ “	?	Old	None other than greenish cast
“ “	Baum Oel	?	“	No pinkish coloration
“ “	Huile D'Olive	Marseilles	“	“ “ “
“ “	“ “	?	“	“ “ “
“ “	Provincer oil	?	“	“ “ “
Peanut oil	Arachide oil	France	Fresh	“ “ “
“ “	“ “	?	Fairly fresh	“ “ “ Slightly more yellowish
“ “	“ “	?	Old	No pinkish coloration
“ “	Huile D'Arachides	Bombay	“	“ “ “
“ “	“ “	Mozambique	“	“ “ “ Faintly yellowish
“ “	Arachides (extra raffisque)	?	“	No pinkish coloration
Sesame oil	Sesami oil	France	Fresh	“ “ “
“ “	“ “	N. Y.	“	“ “ “
“ “	Sesam Oel	?	Old	“ “ “

TABLE I (*Continued*).

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Sesame oil	Sesami oil	?	Old	No pinkish coloration
" "	Sesame	Bombay	"	" " "
" "	Sesames (extra Jaffa)	?	"	" " "
" "	Sesame (Brunede Mai)	?	"	" " "
Corn oil	Corn oil	N. Y.	Fresh	" " "
" "	" "	Chicago	Old	" " "
Palm oil	Palm oil	?	"	" " "
Cocoanut oil	Coprah	India	Fresh	" " "
" "	Pure cocoanut oil	P. F. P. Co.[1]	Old	" " "
Linseed oil	Linseed oil	N. Y.	Fresh	" " "
" "	Lein oil	?	Old	" " "
Nigre oil	Nigreseed oil	France	Fresh	Brownish, pinkish coloration
5 per cent of above	In (C. P.) lard			Very faint pinkish coloration
Sunflower oil	Sunflowerseed oil	?	Old	Yellowish, pinkish coloration
5 per cent of above	In (C. P.) lard			Brownish-pink, not a positive reaction
Sunflower oil	Sunflower oil	?	Old	Yellowish, pinkish coloration
5 per cent of above	In (C. P.) lard			Practically no coloration

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[1] Pure Food Product Co., Chicago, Ill.

TABLE I (*Continued*).

6–24

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Sunflower oil	Sonnenblumen Oel	?	Old	Brownish-pink colorat'n (Milleau—Reddish)
5 per cent of above in (C. P.) lard				Practically no coloration
Sunflower oil	Extracted from seed	N. Y.	Fresh	No coloration (Milleau—No col'rat'n)
Rape or colza oil	Rape seed oil	N. Y.	Fresh	Slightly brownish-pink (Milleau—Brownish coloration)
5 per cent of above in (C. P.) lard				Practically no coloration
Rape or colza oil	Huile de Navetto	?	Old	No coloration
" " "	Extracted from seed	N. Y.	Fresh (A) and (B)	No coloration whatever
Poppyseed oil	Mohn Oel	?	Old	Brownish-yellow; not a C. S. oil coloration (Milleau—Reddish coloration)
5 per cent of above in (C. P.) lard				Practically no coloration
Poppyseed oil	Pavot de l'Inde	?	Old	No coloration
" "	Extracted from seed	N. Y.	Fresh	No coloration whatever
(Cow) butter	Butter	Local stores	Fresh	No coloration.
" "	"	Elgin make	?	Coloring in butter masks any coloration possibly produced
" "	"	Home-made	Fresh	No coloration
Beef fat	Tallow (Prime)	Chicago	"	No change from original color
" "	" (No. 1)	"	"	No change from original color
" "	Oleo Stearine	"	"	No pinkish coloration
Hog fat	Lard (Prime Steam)[1]	"	"	" " "

[1] Of about 500 commercial samples with this method only 5 or 6 gave colorations.

Table I (*Continued*).

Sample of	Marked	Purchased at	Condition.	Coloration produced.
Cottonseed oil	C. S. oil, 'White'	American Mills	Fresh	Deep crimson coloration
" "	" " 'Yellow'	"	"	Deep crimson coloration (slightly darker than above)
" "	" " 'Crude'	"	"	Deep crimson coloration (darker than above)
" "	" " 'Winter'	"	"	Deep crimson coloration
" "	" " 'Summer'	"	"	Deep crimson coloration (slightly lighter than above)
" "	" " 'Stearine'	"	"	Deep crimson coloration (lighter than above)
" "	Extracted from seed	"	"	Deep crimson coloration
" "	C. S. oil	"	Old (7 years)	No pinkish coloration
" "	" "	"	" (5½ ")	Reddish-yellow coloration, not proper cotton oil coloration
" "	Cotton oil stearine	English Mills	Old (decomposed)	No coloration
Rosin oil	Rosin oil	?	?	No change in color
Mineral oil	Oil petrole	N. Y.	Fresh	" " " "
" "	Vaseline oil	?	Old	" " " "
Dégras	Degras	?	?	" " " "
Engine oil	Engine oil	N. Y.	Fresh	" " " "
Thran or blubber oil	Menhaden oil	"	?	" " " "
Soap	From cotton oil	American Mills	Fresh	Deep scarlet coloration (slightly more yellowish than with oil).
Fatty acids	From above	"	(Undried)	Deep scarlet coloration (slightly more brownish than with oil)

TABLE II.

Results with Pure Lards and Adulterants, Etc.

Sample of	Coloration produced.
Pure lard	No coloration
Soap from pure lard	No coloration (other than the cream color of soap)
Fatty acids from above	No coloration (other than the cream color of acids)
Pure lard blown with air, 10 hours[1]	Yellowish coloration after 6 to 7 hours boiling
Pure lard blown with air, 18 hours	Yellowish coloration after 6 to 7 hours boiling
Pure lard blown with air, 24 hours[2]	Slightly cream coloration in 5–6 hours (continued boiling gives maroon color—abnormal test)
Pure lard containing starch	No coloration
" " " resin (Colophony)	" "
Pure lard containing glycerin	" "
" " " chlorophyl	" change in color
" " " Fuller's earth	" coloration
Pure lard containing salt (NaCl)	" "
Pure lard containing chlorine (Cl)	" "
Pure lard containing boric acid	" "
Pure lard containing salicylic acid	" "
" " " curcuma	" "
" " " annatto	" "
" " " " carrotene "	" change in color
" " " saffron leaves	" " " "
" " " "annatolene"	" " " "
" " " yellow wood	" coloration
" " " butter color " R"	" change in color
Pure lard containing butter color " Y"	" " " "
Pure lard containing oleaginous annatto	" " " "

[1] Free fatty acids, 0.9 per cent.

[2] Free fatty acids, 6.2 per cent.

TABLE III.

Results as to Sensitiveness of Reaction.

Sample of	Time of test.	Coloration produced.
Pure lard[1]	3–4 hours	No coloration
" "	10 hours	Maroon coloration, not that of a cotton oil (due to overheating—abnormal test)
" " +1 per cent cotton oil	15 minutes	A pink coloration
" " +½ " " "	15 "	" " "
" " +½ " " "	30 "	Quite reddish coloration
" " +¼ " " "	15–30 minutes	Faint coloration
" " +⅛ " " "	2½–3 hours	" "
" " +1/10 " " "	"	Very faint coloration
" " +1/16 " " "	3 hours	Doubtful "
" " +1/16 " " "	4–5 hours	Slight pinkish coloration as compared with blank
" " +1 " " "	15–30 minutes	No color in steam-bath
" " +1 " " "	" "	Quite pinkish in salt-bath
" cottonseed oil		Pinkish in steam-bath in few minutes
Soap from lard with 1 per cent C. S. oil	2–3 hours	Brownish-yellow coloration, no positive indication
Fatty acids from above	"	No coloration other than that of acids
Soap from lard with 2 per cent C. S. oil	"	Brownish-red, not good C. S. oil coloration
Fatty acids from above	"	Not a positive indication
Lard with 2 per cent C. S. oil		Pinkish in few minutes
Compound lard (high per cent C. S. oil)		" " " "
Soap from above	"	Reddish-yellow to scarlet, fairly good indication
Fatty acids from above	"	Deep scarlet, very good indication
"Cottolene" lard compound 4–5 years old, center of package	"	Deep scarlet color
Above sample, surface of package	"	Yellowish-red, not a good positive indication

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[1] See foot-note, p. 365.

TABLE IV.

Effect of High Temperatures.

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Cottonseed oil	150° C.	0[1]	Glass	Normal deep coloration
" "	150° C.	½–1 hour	"	Doubtfully lighter coloration than above
Above sample	175° C.	0	"	Same as above
" "	175° C.	½–1 hour	"	" " "
" "	200°	0	"	About same as above
" "	200°	1–2 hours	"	Considerably lighter coloration than above
" "	225°	0	"	Still lighter and yellowish, not a good coloration
1 per cent C. S. oil in lard	Normal		"	Good indication
1 " " " " "	150°	0	"	Doubtfully lighter reaction
Above sample	150°	½–1 hour	"	Same as above
" "	175°	0	"	Faintly lighter reaction than above
" "	175°	½–1 hour	"	Considerably lighter reaction than above
" "	200°	0	"	Only faint coloration (2–3 hours boiling)
" "	200°	½–1 hour	"	No coloration (identity of oil destroyed)
Fresh sample oil	250°	0	"	Possibly lighter reaction than with original oil

[1] Merely brought up to the temperature, not held there.

TABLE IV (*Continued*).

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Fresh sample oil	275°	0	Glass	Slightly lighter reaction than above
“ “ “	300°	0	“	Somewhat “ “ “ “
“ “ “	300°	15–30 minutes	“	No coloration (identity of oil destroyed)
Fumes from above				No coloration
Fresh sample oil	315°	0	“	Only slight coloration
“ “ “	320°	0	“	No coloration
“ “ “	325°	0	“	“ “ (after 1 hour boiling)
“ “ “	308°	0	Glass (in vacuum)	Fairly strong coloration
“ “ “	315°	0	“ “	No coloration
“ “ “	250°	0	Nickel	Faint coloration
“ “ “	275°	0	“	No coloration
“ “ “	295°	0	“	“ “
“ “ “	275°	0	Iron	Strong coloration
“ “ “	300°	0	“	No coloration
“ “ “	140°–150°	1 hour	Steel	“ “
“ “ “[1]	200°–210°	1 “	Porcelain	Good coloration, little affected
Fresh sample oil + pieces of copper	175°	0	Glass	Coloration
Fresh sample oil + pieces of copper	200°	0	“	No coloration
Fresh sample oil + pieces of iron	285°	0	“	Only slight coloration
“ “ “ + “ “ “	308°	0	“	No coloration

[1] After frying batch of crullers.

TABLE IV (*Continued*).

Sample of	Temperature subjected to.	Time held.	Quality of vessel.	Coloration produced.
Fatty acids of C. S. oil	110°	12 hours	Glass	Only slightly lighter reaction than undried acids
" " " 1 per cent C. S. oil in lard	Normal		"	No positive indication
Fatty acids of 1 per cent C. S. oil in lard	110°	12 "		No indication of cotton oil (acids darkened)
Fatty acids from C. S. oil soap stock	Distilled	?	?	No indication of cotton oil
Cottonseed oil	"	?	Glass	" " " " "

TABLE V.

Miscellaneous Experiments.

Experiment.	Coloration produced.
Cottonseed oil + amyl alcohol ($C_5H_{11}OH$) boiled	No coloration
“ “ + CS_2 (pure) boiled	“ “
“ “ + “ + 1 per cent S boiled	Slight coloration (yellowish-brown)
“ “ +(“ + 1 “ S) + ethyl alcohol (C_2H_5OH) boiled	Better coloration, not the vivid coloration
Cottonseed oil + (CS_2 + 1 per cent S) + amyl alcohol boiled	Good characteristic coloration
(Lard + 1 per cent C. S. oil) + (CS_2 + 1 per cent S) boiled	No coloration
(Lard + 1 per cent C. S. oil) + (CS_2 + 1 per cent S) + C_2H_5OH boiled	“ “
(Lard + 1 per cent C. S. oil) + (CS_2 + 1 per cent S) + $C_5H_{11}OH$ boiled	Good reaction
C. S. oil + $C_5H_{11}OH$ + CS_2 (pure) boiled	Only pale coloration
Above test + free S boiled	Deep coloration
C. S. oil + $C_5H_{11}OH$ boiled	No “
Above + free S boiled	“ “
“ + CS_2, boiled	Deep coloration
1 per cent C. S. oil in lard, regular test	Good “
1 “ “ “ “ “ + 5 per cent S regular test	No improvement in coloration
C. S. oil, regular test	Deep coloration
Above test + copper and boiling	No change of coloration
C. S. oil blown with air several hours regular test	“ “ of reaction

From the foregoing it appears that the Halphin test, if conducted properly, proves to be thoroughly characteristic of cottonseed oil and is evidently one of the most valuable color tests known for the identification of cotton oil in other oils and fats.

THE W. J. WILCOX LARD AND
REFINING CO., N. Y.

APPARATUS FOR GENERATING GASES AT CONSTANT FLOW AND OF HIGH EFFICIENCY.

BY GEORGE A. KOENIG.

The question of how to supply school laboratories with hydrogen sulphide in the least objectionable way is still open for discussion. Many of the best equipped laboratories have each desk provided with the gas in a well-ventilated small hood. Aside from the first cost of such an arrangement, it seems to me to tend to wastefulness on the part of the student. He detaches the rubber tube but forgets the closing of the stop-cock. Or he may let the gas go through a solution for hours, when a few minutes would have been sufficient. Similar objection attaches to the Kipp apparatus in addition to the variation in the flow of gas and the imperfect utilization of the acid. In recent years several styles of apparatus have been described which mark good progress in the right direction. There is, however, still room for improvement. When I took charge of the Department of Chemistry in the Michigan College of Mines, in 1892, I found the laboratories very imperfectly ventilated: the Kipp apparatus in the same hood that served for evaporations, and frequently no draught in that hood. A radical change was too expensive to be practical at the time. Two hoods were put into each laboratory 8 inches deep and 6 feet wide, the draught pipes leading directly near the ridge pole of the building. Draught was created by one burner at the throat of the hood. This arrangement satisfied the demand of ventilation fairly well. In order to counteract the waste of the materials in the Kipps, each hood was provided with two generators essentially of the form shown in the figures: 1. A narrow glass tube 350 mm. long, drawn to about 8 mm. at the bottom. At the top a two-

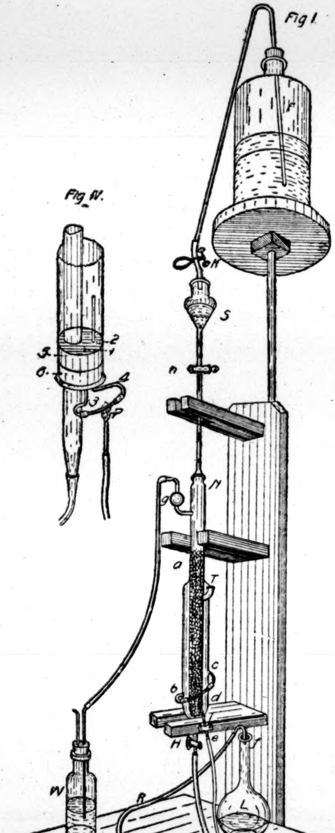
Fig I.
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Fig IV.
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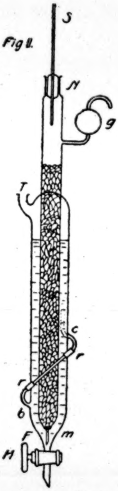
Fig II.
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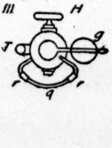
Fig III.
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q

hole rubber stopper with the stem of a separatory funnel through one hole and a gas delivery tube through the second hole. The stem is about 200 mm. from stop-cock to outflow. On the length of this stem depends the possible inside pressure; the length mentioned satisfies all laboratory demands. The lower end is furnished with the rubber U-tube *R*, Fig. I., and the tube must be sufficiently long to permit a difference of level equal to the length of the stem of the separatory funnel. The generating tube is provided with a disk of copper wire gauze and stem at *m*, Fig. II., and then filled with ferrous sulphide. Now, if the bulb of the funnel *s* holds 50 cc., it is evident that no more acid can be wasted than one filling without refilling the bulb by pressing on the pinch-cock *k*, Fig. I. The stop-cock *h* regulates the outflow of the acid. Here the student may wilfully waste by turning on full instead of 1 drop a second. But he cannot waste much. In fact the gas will be generated so violently, if he turns on full, that he will become alarmed, as I have noticed on several occasions, and he will turn off in most cases. The outflow of the stem should be drawn to 1 mm., in order that a small drop may form. Were it not for the unavoidable minute solids in the dilute acid, a narrowing to 0.5 mm. would be preferable. This clogging happens mostly in the stop-cock *s*, and is the only objectionable feature in my scheme. In most cases a quick turn to full flow, several times repeated, will remove the clogging matter; but sometimes the pushing through of a thin wire is needed.

The hot-water jacket was added in the first place for generating chlorine gas with this apparatus. But last winter, in February, when the temperature of the rooms fell to near freezing-point during the night, the hydrogen sulphide generators refused to start in the morning, the dilute cold acid being without effect upon the iron sulphide, then the jacket was added. The result has been so satisfactory that a temperature of about 80° C. is maintained now in all generators. The water-jacket should be of glass; spilling of acid is unavoidable, and corrosion of any metallic tube would be certain; moreover, the decrease in the column of ferrous sulphide should be visible.

Fig. IV. shows a simple way of constructing a tight jacket. The generating tube being 25 mm. wide, the jacket tube is 45 mm. The rim of the latter is flared outwards. A cork stopper (5) is fitted to slide into the tube tightly. The stopper is bored eccentrically for the generator tube, leaving room for the small borings (1) and (2). Push this stopper into position, 30 mm. above the rim, insert the generator tube and the small tubes so that (1–3) is just even with the inner disk, whilst (2–4) projects above this disk about 40 mm. Either tube is bent at right angles, the one at (3) the other at (4), and there is a second short bend so that the piece 9 can be inserted between the ends by means of short rubber connections (*z*,*z*, Fig. III.). 9 is bent to be concentric with the jacket, and must stand off at least 30 mm. The bend at (3) is 25 mm. below the rim of the jacket, whilst bend (4) is tangent to it. The piece (9) is about 80 mm. long and 5 mm. wide (outer diameter). This piece, after being fitted into place, forms an incline (Fig. II.). When all the pieces are in proper position, reverse the tube and pour into the space (6) properly moistened Portland cement of the consistency of thick mud. Stir it carefully with a wire to remove air bubbles, and set away two days. Neither sealing wax nor plaster of Paris answer the purpose. Portland cement stands the hot water indefinitely. The upper end of the jacket is best protected by a roof of sheet aluminum against the spilling of acid, which would soon destroy the cement block at the bottom. The roof can be fastened to the generator tube by a rubber band.

The jacket being filled with water, we place a small flame (7) under the boiling-tube (9). (This latter is best made of brass, although I find that a glass tube stands a long time with proper care.) It is evident that a warm water current is established at once, the cold water sinking into (1) and the hot water rising through (2) to the upper jacket. The burner consists of a 5 mm. glass tube and the flame is about 12 mm. high, later only 6 mm., when the jacket has assumed the proper temperature. Figs. I., II., and III. represent the apparatus entirely of glass. The rubber stopper is done away with, its place being taken by a ground glass stopper *N*, which is melted into the stem of the separatory funnel. The arrangement of the boiling tube explains itself from the drawing. Generating tube and jacket are fused together above and below. The tubulature (*T*) serves to fill water into the jacket. The glass stop-cock (*H*) at the outflow of the generating tube was introduced to do away with the rubber tube *R*. This was not found to be feasible, because the very narrow opening fills up at once with the fine particles of the generating body. The bore in the cock must not be under 5 mm. This stop-cock has proved serviceable in other ways. Whenever the apparatus is to be taken from the stand the cock is closed and all dripping from the rubber tube is thus avoided.

The iron sulphide should be screened after crushing or granulating, and only those pieces should be charged into the generator whose average diameter lies between 3 mm. and 10 mm. The charging is done with a funnel made from sheet aluminum after lifting out the stopper at N. The tube being filled up to the goose-neck, the apparatus will work steadily for one working day without perceptible lessening of the constancy of the gas current, although the economy in acid will diminish. The tubes in my laboratories are charged every morning.

When the apparatus is to be used for the generation of chlorine, the column of manganese dioxide should not be higher than one-third of the available tube. The concentrated hydrogen chloride should be diluted with enough water to raise the boiling-point to 80° C. Under such conditions a chlorine current can be maintained of extraordinary constancy. The pyrolusite should be screened to pieces between 2 mm. and 5 mm.

MICHIGAN COLLEGE OF MINES,
June, 1900.

REPORT.

International Atomic Weights.

Near the close of the year 1897, the German Chemical Society appointed a committee to select atomic weights for common use in Germany. The confusion arising from the use of different values, and especially of different standards of reference, had become unbearable. After nearly a year's deliberation, they announced their conclusion that it is expedient to call oxygen exactly 16, and to refer other elements to this standard. They published a carefully considered and conservative table of atomic weights,[1] which immediately gained wide acceptance, partly because of its intrinsic merits, and partly because it was vouched for by such eminent men as Landolt, Ostwald, and Seubert. At the close of the remarks accompanying this table, the three members of the committee expressed the hope that the matter might be clinched by international agreement. The hope was strengthened by the fact that the two other modern tables, those of Clarke and of Richards, differed but slightly from the table presented in Germany. Time has strengthened this hope still farther, for the two subsequent yearly editions of the three tables have steadily tended towards the elimination of earlier differences, until now they are even more alike than they were at first.[2]

On March 30, 1899, having been encouraged by the favorable reception of their work, the German Committee issued, to all important associations interested in chemistry throughout the world, a general invitation to appoint delegates to an International Committee.[3] The number of delegates was not determined, and the outcome was the appointment of 57 men from among the most eminent chemists of 11 nations. As representatives on this International Committee, the American Chemical Society appointed Professors F. W. Clarke, J. W. Mallet, E. W. Morley, T. W. Richards, and E. F. Smith. Shortly afterward the American Academy of Arts and Sciences added Professors Wolcott Gibbs and Ira Remsen to the list of American delegates. Besides these 7 men, the present International Committee contains 15 from Germany, 11 from Austria, 8 from England, 5 from Belgium, 3 each from Switzerland and Italy, 2 from Japan, and 1 each from Holland, Russia, and Sweden. It is much to be regretted that Denmark, France, and Norway have as yet made no appointments.

Having thus received very general support, the German Committee, in October, 1899, decided upon another step. They forwarded to each member of the International Committee a circular letter containing three questions, which were speedily answered by nearly all of the delegates. A literal translation of these questions follows:

"1. Shall $O = 16$ be fixed as the future standard for the calculation of atomic weights?

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[1] Ber. d chem. Ges., **31**, 2761 (1898).

[2] See J. Am. Chem. Soc., **22**, 78 (1900); also Proc. Am. Acad., **35**, 621 (1900) and Ber. d. chem. Ges., **33**, 1 (1900).

[3] Ber. d. chem. Ges., **31**, 2949 (1898); **33**, 1847 (1900).

"2. Shall the atomic weights be given with so many decimals that the last figure is certain within half a unit, or what other procedure shall be adopted?"

"3. Is it desirable that a smaller committee should be formed, which should undertake the continual revision of the yearly atomic weight table and its publication? In case of agreement upon this point it is proposed that each association shall name a single delegate to this smaller committee."

The 49 answers to these questions are highly interesting.[1] As regards the first question, only 7 chemists (1 American and 6 Germans), were decidedly in favor of retaining hydrogen as the standard, while 40 were decidedly of the opposite opinion. Two were willing to accept either or both standards of reference. In spite of the fact that men as eminent as Professors Mallet, Volhard, Winkler, and Wislicenus are in the minority, the majority is so overwhelming that we must look upon this point as settled for a long time. Even if the probable delegates from the unrepresented countries should all vote in the negative, the majority must remain in favor of $O = 16.000$. Thus the new term "international atomic weight" is perfectly clear and unequivocal in its meaning as to the standard of reference, and an important step has been taken.

It may not be irrelevant here to enumerate the advantages and disadvantages of this international standard. In the first place, it is evident that the question is a practical one, not a theoretical one. If Prout's ancient hypothesis seemed at all probable, there would indeed be a strong reason for assuming hydrogen as unity; but Prout's hypothesis cannot now claim serious consideration, at any rate in its original form. No other theoretical reason for calling hydrogen exactly 1.000 is known to me. What, then, are the relative *practical* advantages to be gained by taking hydrogen or oxygen as the standard? In the first place, the precise quantitative analysis of compounds containing hydrogen is a very difficult matter, and water is the only one which has been adequately studied. Hence nearly all atomic weights must be referred to hydrogen through the medium of oxygen; and if the ratio $H:O$ is found to be even a little in error, all other values must be recalculated. Morley's work on this ratio is indeed magnificent, and it is not likely that his accuracy can be surpassed for a long time; nevertheless the principle still remains. Oxygen on the other hand has been directly compared with many metals, as well as with potassic chloride and similar salts obtainable from the chlorates and their analogues. Hence from the point of view of directness of comparison, oxygen is to be preferred. Silver might be even better, as Erdmann and Volhard point out in their replies to the circular letter; but the question does not concern the starting of an entirely new system, but rather the choice between the two old ones.

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[1] Ber. d. chem. Ges., **33**, 1853 (1900). The answers are published in full.

Another point to be considered is the effect of the decision upon the data contained in the past literature of chemistry. Any change which tends to confuse the understanding of the work of the past would be indeed a grievous one; and a change to $O = 15.879$ could not but have this effect. Little or nothing has been written with the assumption of this standard, while a great bulk has been written with the assumption $O = 16$. The confusion caused by the inaccurate value $O = 15.96$ is quite bad enough, without the introduction of a new stumbling block. Moreover, in the gas-constant and a multitude of other physico-chemical constants the value $O = 16$ enters, and a change in this standard would complicate the use of a great mass of valuable literature of this kind.

Another, although somewhat trivial, reason why oxygen should be taken as 16 is because in that case a somewhat larger proportion of the atomic weights approximate whole numbers than would be the case otherwise.

The chief objection to the proposed standard is a pedagogical one. It is claimed that confusion is caused in the mind of the student by the use of the number 1.0075.[1] The German Committee points out in its last report that this difficulty may be avoided by giving the elementary student only the round numbers (which suffice amply for his purpose), accompanied by the statement that these are rough approximations. There is obviously another way of avoiding the confusion, and that is by doing away with hydrogen as a standard of specific gravity. The difficulty of preparing this gas in a pure state, and its great lightness are arguments against it, in any case. Moreover, in my experience the simplicity of the relationship between the specific gravity referred to hydrogen and the molecular weight is quite as likely to be a stumbling block as an assistance. Many a beginner learns by heart the statement that the specific gravity is twice the molecular weight; for he does not pause to think about it and see that he has inverted the ratio. If on the other hand the specific gravity of oxygen is taken as the standard, the adverse arguments disappear, and even a dull student can hardly forget the reason why the specific gravity of the gas X referred to oxygen must be multiplied by 32 to give the molecular weight. For several years I have used this method with large classes, and find that it gives no trouble. The only data needing recalculation are the specific gravities of the gases, and that is a simple matter. It seems to me, by the way, that the use of 2 instead of R in physico-chemical formulae has the same pedagogic fault of obscuring the source and nature of the symbol, as this use of 2 for the molecular weight of hydrogen.

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[1] Much has been written upon both sides of this question. Besides the articles already referred to, many references may be found in two papers by Küster and Brauner [Ztschr. anorg. Chem., **14**, 251 and 257 (1897)].

The answers to the second international question, which seeks to determine the number of decimal places to be given, support the German Committee in its position with a majority almost as overwhelming as in the case of the first question. The minority of 8 consists of 3 Americans, 3 Germans, and 2 Japanese, all the others desiring to omit all figures which are not certain to within half a unit. The committee in summing up the opinion upon this subject states that its desire is to propose a table for common use, and that the minority, which desires the retention of one uncertain decimal place, has rather had in mind the requirements of work of the greatest precision. Undoubtedly the curtailed table will answer for most purposes, but it seems to me that the nature of the decimal notation causes an unfortunate incompleteness in it. Although in the face of so great a majority, this matter, like the other, must be considered as settled, I am tempted to call attention to this incompleteness in relation to numercial data of all kinds.

Let us consider a concrete example—the case of nitrogen. Few would be willing to contend that the last figure in the number 14.04 is certain. Let us assume, for the sake of argument, that this atomic weight may really be as low as 14.034 or as high as 14.046. According, then, to the rule which has just been adopted by the International Committee, the figure 4 should be omitted, and nitrogen should be called 14.0. Such an omission causes an error far greater than the uncertainty which leads to the dropping of the figure. The uncertainty named above is only 0.04 per cent, but the minimum error in the value 14.0 is 0.24 per cent, if the lower value given above is supposed to be the lowest possible. Clearly one must either record uncertain figures, or else omit figures which have a real significance. The dropping of a decimal place at once reduces tenfold the power of a number to express slight changes of value ; but numerical results may have any degree of accuracy, and cannot be placed strictly in classes separated by gaps so wide. For this reason it is a well-known practice in scientific calculation to retain during the calculation one uncertain figure, while a final result is often relieved of this uncertain figure. According to this rule, the table of atomic weights should always give an uncertain figure in each value, for atomic weights are simply data for further calculation. If this is done, the user has all the truth, and may reject as much of it as his occasion permits. Such a table of atomic weights seems to me to be the best, because it is capable of fulfilling all uses.

Quite another point of view should be adopted in making a table solely for common use. Here we are concerned not with the number of exact figures which may have been determined by Stas, but rather with those figures which will have an influence upon the work in hand. Usually the error in such a value is important not on account of its absolute magnitude, but rather on account of its relation to the value itself. In short, the percentage error is that which ought to be considered in constructing a table of atomic weights for common use. A majority of chemists would probably decide that a table in which the numbers were within 0.1 per cent of their true values would serve all ordinary purposes. Most common methods are not able to attain as great a degree of accuracy even as this, but the admission of a wider range of inaccuracy in a table of atomic weights might by summation cause an appreciable error.

Silver might be called 108.0, chlorine, 35.5, bromine, 80 0, iodine, 126.9 potassium, 39.2, sulphur, 32.1, and lead 207.0 without seriously affecting the results of most quantitative work, and indeed everyone frequently uses such approximate values. Even in this approximate table hydrogen should be 1.008, and not 1.01, however, if the percentage rule is to be followed.

The last question asked by the German Committee, suggesting the appointment of a small standing committee, was answered affirmatively by every one. The original plan of having a representative from each society would evidently result in the formation of an unwieldy body, hence the German Committee has wisely concluded that a small number, perhaps three, should be elected from among those who have had especial experience in the matter of atomic weights.

The matter is by no means finished. The German Committee asks anyone who has anything new to say upon the questions under consideration to send a brief statement of his views to Professor Landolt before Nov. 15th, and some new ideas may have been advanced in the discussion in Paris at the end of July. The balloting for the smaller International Committee is now taking place. The German Chemical Society, and the members of its committee, are greatly to be congratulated on the success of the undertaking. Much progress has already been made in a matter important not only in itself, but also in its relation to the growing international scientific understanding. THEODORE WILLIAM RICHARDS.

MT. DESERT, MAINE,
August 6, 1900.

REVIEWS.

COMMERCIAL ORGANIC ANALYSIS. BY ALFRED H. ALLEN, F.I.C., F.C.S. Third edition, illustrated, with revisions and addenda by the author and HENRY LEFFMANN, M.A., M.D. Volume I: Introduction, Alcohols, Neutral Alcoholic Derivatives, Sugars, Starch and Its Isomers, Vegetable Acids, etc. Philadelphia: P. Blakiston's Son & Co. 1898. pp. 557. Price $4.50.

Volume II, Part II: Hydrocarbons, Petroleum, and Coal Tar Products, Asphalt, Phenols and Creosotes, etc. 1900. pp. 330. Price, $3.50.

This work has been so long a standard one, and is so extremely useful for the subjects of which it treats, that all chemists will welcome a new edition. While the appearance of an unauthorized reprint of an older edition may be considered as an excuse for haste in getting out the first volume, it is unfortunate that time could not have been taken for a more thorough revision. In a number of cases erroneous statements, which might have been easily corrected by reference to recent standard works on organic chemistry, have been allowed to stand. Thus, on p. 232, an old and incorrect equation is given for the formation of chloroform from alcohol. On p. 243 sugars are defined as polyatomic alcohols and so many misleading and erroneous statements are included in the classification which follows as to make that portion of the book almost useless. The practical treatment of the analysis of sugars, which is, after all, much more vital to the usefulness of the book, is more satisfactory. The material which is given could have been made much more easily available, however, by careful digestion and rewriting in such a manner as to incorporate the new portions with the old.

The revision of the second part of the second volume has been more complete and a large amount of new and useful matter has been added. The reactions upon asphalt and upon phenols have, especially, been largely increased. Some errors are, of course, to be found, but these are, mostly, of such a nature as not to impair the book seriously for the practical purpose for which it is intended. The claim of the preface that the nomenclature of the Geneva convention has been applied is not justified by an examination of the text. In the classification on p. 18, ethyl, propyl, and similar radicals are spoken of as hydrocarbons. The erroneous statement that hydrogen is found in natural gas is given and illustrates the difficulty of correcting an error which has found its way into text-books.

While criticizing minor defects it would be unjust not to emphasize the fact that the general excellence of the work is such as to make it almost indispensable to any chemist working in this field. W. A. N.

THE MANUFACTURE OF VARNISHES, OIL CRUSHING, REFINING AND BOILING, AND KINDRED INDUSTRIES. Translated from the French of ACH. LIVACHE, Ingénieur Civil des Mines, greatly extended and adapted to English practice, with numerous original recipes, by JOHN GEDDES MCINTOSH, Lecturer and Demonstrator on the Manufacture of Painters' Oils, Colors, and Varnishes, Regent Street Polytechnic. London: Scott, Greenwood & Co. 1899. New York: D. Van Nostrand Co. pp. vii + 403. Price, $5.00.

This book includes in its general scope a description of the sources and character of the raw materials used in making varnishes, together with some account of methods of manufacture and of processes for the qualitative and quantitative examination of the various substances involved.

From the chemical standpoint the book leaves much to be desired. Many erroneous statements are made which indicate ignorance or carelessness. Thus, on p. 88, a statement is given which implies that picrate of ammonia is formed by neutralizing picric acid with soda. On p. 105, amyl acetate is said to be formed by heating amyl iodide to 120° C. with silver nitrate. Occasionally antiquated names or even antiquated formulæ are used; as sulphovinic acid for ethylsulphuric acid or the acid ethyl ester of sulphuric acid, and EtO_2Na for sodium ethylate.

The accounts of raw materials and of processes of manufacture are fairly satisfactory. The directions for analysis are, however, often so concise that a chemist unacquainted with the methods used with this class of materials would find some difficulty in following them. W. A. N.